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DEVELOPMENT OF SYNTHETIC THICKENER FOR PIGMENT PRINTING AS A SUBSTITUTE OF KEROSENE OIL

A MAJOR PROJECT REPORT
SUBMITTED TOWARDS THE PARTIAL FULFILMENT OF THE
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Submitted By
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APRIL 2001

DEDICATED

TO

MY PARENTS

CERTIFICATE

This is to certify that the research project entitled "Development of synthetic thickener for pigment printing as a substitute of kerosene oil' submitted by Mr. Yogesh Kumar Agarwal, for the award of the degree of Master of Engineering in Polymer Technology. This is a bonafide record of the research work carried by him under the guidance and supervision of the undersigned.

The results contained in this project work are original and have not been submitted to any other university or institute for the award of any degree or diploma to the best of our knowledge.

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TO WHOMSOEVER IT MAY CONCERN

This is to certify that the research project entitled "Development of synthetic thickener as a substitute of kerosene oil" submitted by Mr. Yogesh Kumar Agarwal to Delhi College of Engineering, Delhi for the award of the degree of Master of Engineering, in Polymer Technology, is a record of bonafide research work carried out by him at R&D centre, Vam Organic Chemicals Ltd., Gajraula. He has worked under my guidance and supervision from 1st October 2000 to 31st March 2001.

The results contained in this project work are original and have not been submitted to any other university or institute for the award of any degree or diploma to the best of my knowledge.

I wish him every success in his career.

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(YOGESH KUMAR AGARWAL)

ABSTRACT

The origin of this study lies in the development of a substitute of kerosene emulsion thickener used in pigment printing. Kerosene has the disadvantages like air and water pollution, risk of fire and inadequate availability. Generally, the copolymers of acrylic/methacrylic acid and alkyl acrylate and their crosslinked products are used as synthetic thickeners.

Copolymers of methacrylic acid-ethyl acrylate were synthesized with varying mole ratio and varying cross linking density with allyl methacrylate as crosslinking agent using solution polymerization technique. Toluene was used as the solvent. The copolymers obtained were characterized by acidimetric and I.R. studies. Rheology of these polymers was studied extensively and found that Brookfield viscosity of the Swollen gels of these polymers is sensitive to shear rate, polymer concentration, pH and electrolytes. Pseudoplastic behaviour of these polymers confirmed their suitability for pigment printing applications. The best polymer was selected for pigment printing. Its performance in pigment printing of cotton was evaluated in terms of colour value, wash fastness, rubbing fastness and handle of the fabric using four pigments. The polymer performs good as synthetic thickener.

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CHAPTER - 1

INTRODUCTION AND LITERATURE SURVEY

1.1 INTRODUCTION

Thickener is an integral and critical part of the print composition in textile printing. Over all print performance of the printed fabric depends significantly on the choice of thickener system. Requirements of thickener properties vary with the application. Viscosity development is the prime requirement of any thickener [1].

Pigment printing of textiles is the simplest and cheapest among all the known printing methods. After drying and heat fixation, the printed articles become ready to meet the customer requirement. As the after wash process is not required for pigment printed products, the process has an edge over other textile printing processes.

The print paste for pigment printing generally contains [2] :

(a) Thickener, (b) Binding agent, (c) Emulsifier,

(d) Pigment, (e) Cross linking (fixing) agent, (f) Softener,

(g) Antifoaming agent.

In pigment printing, it is necessary for printed pastes to be pseudoplastic i.e. their viscosity should decrease under shear and redevelop when shear is removed so that they can be applied on textile material easily.

In printing of textiles with different classes of dyes, different types of thickener systems are recommended depending on their compatibility with dyes [3]. For many years the thickener [4] requirement of textiles printers have been met by naturally occurring gums such as guar gum, alginate,

locust bean gum, starch and cellulose derivatives [5]. All these natural product based thickeners are being used for printing with reactive as well as disperse dyes. Natural thickeners used for pigment printing [6] do not give satisfactory results in terms of depth of color, brilliance of color shade, handle of the fabric and wash fastness. Pigment printing became a successful process only with the introduction of emulsion thickeners. In such a thickener, two liquids that are mutually insoluble (e.g. kerosene and water) are thoroughly stirred together with an emulsifying agent. A high viscosity is obtained.

Emulsions in which kerosene forms the inner phase are termed oil-in-water (o/w) emulsions and those in which water forms the inner phase, water-in-oil (w/o) emulsions. Both are used in the textile industry. Emulsion thickeners give better color yield and brilliance than the water-soluble thickeners and have no effect on the handle and fastness, since both phases in the thickener are easily removed by heating [7].

Although oil-in-water emulsion gives excellent prints, the use of such a large amount (80-85%) of kerosene/while spirit can create following major problems.

1. Risk of explosion during drying of fabric in drier.
2. Use of volatile solvents leads to air and water pollution.
3. Wasteful use of energy.
4. Increases in the prices of all petrochemical products make pigment printing costly.

Increasing awareness regarding environmental protection, safety and subsequent stringent regulations have forced the processors to shift to eco-friendly systems for thickening. A great deal of research has been

carried out in the past two decades on synthetic thickeners for economic and ecofriendly reasons. The most significant have been in the field of pigment printing and many reviews dealing with natural and synthetic thickeners have been published [6,8-11]. Successful use of aqueous system for pigment printing and its beneficial effect on safety, environmental pollution and economy of operation has given added impetus to the use of synthetic thickeners. Synthetic thickeners are high molecular weight polymers contain an acidic monomer such as acrylic, methacrylic or maleic acid etc. as an essential component [12].

Different systems have been developed replacing kerosene partially or completely and are being used commercially. Among them acrylic based thickeners are widely used. The commercially available acrylic based thickeners being used in India are RAN 5000 (RSA Polymers) Carbopol 846 (B.F. Goodrich), Alcoprint PTF (Allied Collids), Lutexal HSF (BASF) and Novaprint (Sigma). Carbopol 846 and Novaprint are in the form of powder while others are in the form of viscous off-white paste.

1.2 SYNTHETIC THICKENERS

1.2.1 Requirement of an Efficient Synthetic Thickener

The necessity to drastically reduce or to eliminate the use of Kerosene has directed the research towards the development of synthetic thickeners [14]. For a polymer to be effective as a synthetic thickener for pigment printing, it should display following properties:

1. High viscosity at low concentration.
2. Insolubility in water, detergent solution, alkaline wash liquor and dry cleaning solvents.

3. Shear thinning behaviour of viscosity and regain of viscosity upon shear removal.

4. Inertness towards pigments and other essential components of the print paste, e.g. fixer, electrolytes etc.

From the description of the essential features given above we can understand the need to develop a product of high molecular weight displaying pseudoplastic behavior. All of these properties can be tailored in synthetic thickeners to provide a good substitute of Kerosene emulsion thickener. The commercially used synthetic thickeners for pigment printing are available as fluffy white powder or are present as viscous off-white paste of low solid content containing some high boiling liquid.

1.2.2 Chemical Composition

Synthetic thickeners are high molecular weight polymers (Mol. Wt 300,000 to 500,000) containing an acidic monomer as an essential component which is a major component responsible for viscosity development. Basically, acrylic based thickeners are copolymers or terpolymers of acrylic acid, methacrylic acid and their esters e.g. ethyl acrylate, butyl acrylate etc. The acid comonomer is responsible for thickening effect and development of viscosity on partial neutralization with a base [15]. Neutralization converts the acid groups into carboxylate anions which repel each other, resulting into uncoiling and extension of the polymer chains. These extended polymer chains can not freely slip over each other, thereby develop the viscosity [16]. This reaction is rapid and gives instantaneous thickening.

The thickening ability increases with increase in concentration of the acid monomer. Since the pigment print do not require after wash, the

thickener remains on the fabric, therefore the glass transition temperature (Tg) affects the feel of the printed fabric.

The most commonly used acrylic monomers in the preparation of the synthetic thickener and their Tg of homopolymers are listed in the Table 1.1 [17].

Table 1.1 : Most Commonly Used Acrylic Monommer For Synthetic Thickeners And Tg Of Their Homopolymers

S.No.	Monomer Name	Tg of Homopolymer (^{0}C)
1.	Acrylic Acid	106
2.	Methacrylic Acid	228
3.	Methyl methacrylate	105
4.	Ethyl methacrylate	65
5.	Methyl acrylate	10
6.	Ethyl acrylate	-24
7.	Butyl acrylate	-54

Glass transition temperatures (Tg) reflect the mechanical properties of polymers over a specified temperature range. Below the Tg, polymers are stiff, hard, brittle and glass like, while above the Tg, they are relatively soft and rubber like. Alkyl acrylate monomer impart softness [18] because of their polymers possess low glass transition temperature. Tg of poly ethyl acrylate is -24^{0}C and of poly butyl acrylate is -54^{0}C . As the size of a pendant group in acrylates increases, glass transition temperature decreases [19]. On the other hand, carboxylic acid monomers confer hardness to their copolymers because their Tg's are very high e.g. the Tg of polyacrylic acid is 106^{0}C and of polymethacrylic acid is 228^{0}C. Hence the selection of comonomers and their composition should be optimized to

obtain a synthetic thickener product with suitable rheological properties and glass transition temperature.

Besides alkyl acrylate comonomers acrylamide is also widely used in synthetic thickener composition since its copolymers are soluble in water. However these copolymers increase the tackiness of the thickener. Methyl methacrylate polymers [20] are also used as thickeners and fabric printed with them has good handle, washfastness and colour yield.

Bhagwat and Srivastava [21] have reported the synthesis of acrylic polymers, to be used as thickeners, by emulsion and solution polymerization. On the basis of their performance in pigment printing of cotton, these polymers have been found to be promising substitute of Kerosene emulsion in pigment printing, either partially or fully.

Crosslinkable monomers such as Allyl methacrylate (AMA), Divinyl benzene (DVB), Diallyl phthalate (DAP), Ethylene glycol dimethacrylate (EGDMA) and Divinylglycol (DVG) have also been used as one of the components in producing synthetic thickeners. Loosely cross linked polymers can provide printable viscosity at a much lower solid content (0.5 - 2%) compared to linear copolymers (solid content 10-15%). Depending upon the absence or presence of a cross linking agent, these acrylic thickeners can be divided into two categories : alkali soluble and alkali swellable respectively.

The effect of chain branching and cross linking on glass transition temperature (Tg) can be explained in terms of free volume. The higher concentration of chain ends in a branched polymer increases the free volume and lowers Tg, whereas cross linking lowers free volume and raises Tg [22].

Pseudoplasticity (shear thinning index) is higher for cross linked polymer compared to linear polymers. The thickening ability increases with the increase in concentration of cross linker upto a certain extent. The amount of cross linking agent and its chemical nature significantly influence its performance as a thickener for textile printing. It was found that the degree of fixation of the dye on the fabric is dependent on the extent of cross linking. Transfer of the pigment from the film of thickener to the substrate was increased by decreasing the extent of cross linking. Hence a highly cross linked polymer can provide high viscosity but at the same time colour value and brightness of printed fabric will be decreased.

1.3 TECHNIQUES OF POLYMERIZATION

The patent literature reveals that copolymers of acrylic have been synthesized by various polymerization techniques like solution [23-29], precipitation [30-31], emulsion [32-47] and inverse emulsion [48-54] techniques as given in Table 1.2. For the application point of view, copolymers in latex form and powder form are effective and easy to use. Powdered synthetic thickener require an initial additional step for the preparation of aqueous dispersion of the thickener in water. By using emulsion and inverse emulsion polymerization technique, the synthetic thickener produced in the form of latex form while by using precipitation polymerization the synthetic thickener produced in the form of fluffy powder.

Table 1.2 Chemical Composition and Synthesis Techniques

Table 1.2(a) Solution Polymerization

Refs.	Monomer(s) (Parts)	Crosslinking monomer	Polymerization conditions	Properties / uses
23	Acrylic Acid (95g)	Benzyl alcohol and allyl glycidyl ether (5g)	Initiator: AIBN (0.05g), solvent: Toluene.	Brookfield viscosity (0.5%, 20 rpm): 38500 cP.
24	Acrylic acid stearyl methacrylate	Allyl Pentaerythirtal	Initiator: lauryl peroxide, solvent : benzene, 80-81^0 C temp.	Brookfield Viscosity (1.2 - 2.0) =4,700-25,000 cP. Used effectively as thickener with reactive, direct and disperse dyes.
25	Acrylic acid (30)	Penta erythritol tetra allyl ether (0.5 g)	Initiator : AIBN (0.3g) solvent : cyclohexane (323 ml), MIBK (17 ml), 60^0 C, 3 hrs.	Brookfield viscosity (20 rpm, pH = 7), = 1500 cP when only MIBK used as solvent.
26	Maleic anhydride (58.84), Isobutylene (50.5), n - Docosyl methacrylate (14.2)	-	Initiator : AIBN, Solvent : ethyl acetate and isopropanol	Mw = 350000, Brookfield viscosity (1% sol., 5 rpm), 30^{0}C) = 2500 cP.
27	Acrylic acid (180g) preneutralized with K2CO3	Divinylglycol (0.09 g)	Initiator : di (2-ethylhexyl) peroxydicarbonate) Solvent : ethylacetate	Particle size < 10 µm, Brookfield viscosity (1% solution, 20 rpm = 59, 200 cP.
28	Tridecyl alcohol ethoxylate (36.8)	-	Solvent : toluene, 80^{0}C, neutralized with glycolic acid	Obtained in solid form used as associative

	Polyethylene glycol (22)		to pH 7 when viscosity reached at 880 Ps. Toluene is distilled off.	thickener.
29	N-N-dimethy acrylamide (7.37) Dimethylamino propyl Methacrylamide (17.58).	PEG dimethacrylate (0.0439)	In 350 g water, Initiator : 2-2' azo bis (2-amidopropane) dihydro chloride, makes a gel	0.5 wt% solution has viscosity 0.3-20 Pas at 25^{0}C at shear rate 1 second 0.01-5 pas at shear rate to sec. Used as cosmetic, pharmaceuticals.

Table 1.2(b) Percipitation Polymerization

Refs.	Monomer(s) (Parts)	Cross linking monomer	Polymerization conditions	Properties / uses
30	Ethyl acetate (638g), Acrylic acid (91g), t-butylacrylamide (39g)	Allylpenta erytrhitol (1.95g)	Initiator : di-(2-ethylhexyl) peroxydicarbonate (0.275g), Solvent: cyclohexane (543g), 45-105^{0}C, time : 8 hrs.	Brookfield viscosity at 20 rpm = 20,000 cPs. Used as thickener for aqs. Compositions
31	Acrylic acid (98.65g)	Pentaerythritol polyallyl ether (0.85g)	Solvent : cyclohexane (735g), 70^{0}C time : 10 hrs, after polymerisation treated with gaseous NH_3 then PEG 400 (32.5g) added.	Powder produced = 122 g. viscosity (0.5 w/w) in water = 21000 cPs (at 20 rpm) used as thickening agent.

Table 1.2(c) Emulsion Polymerization

Refs.	Monomer(s) (Parts)	Crosslinking monomer	Polymerization conditions	Properties / uses
32	Ethylacrylate (192.5), Methacrylic acid (140), N-Decyl acrylamide (17.5)	-	Initiator : ammonium persulfate (0.25% sol. 55g), Emulsifier; Alipal EP 100 (30% sol., 46.7g), water: monomer = 2, 86-90^{0}C.	Yield 100%, suitable for textile printing, cosmetics, oil well drilling muds, etc.
33	Ethylacrylate (100), methacrylic acid (80)	Ethoxylated stearyl alcohol allyl ether (I) (10 mol)	Initiator: ammonium persulfate. (0.5g), Emulsifier Porlankrol ESD (7.5 g), water: 455.8g, 85^{0}C.	Brookfield viscosity = 14,000 cPs vs 60 cPs in the absence of [I].
34	Ethyl acrylate (116), Methacrylic acid (90.5) Amonoester of ethoxylated heptadecanol and methylene succinic acid (23)	DAP (0.3g)	-	For textile printing pastes, adhesives, wall joint compounds, well drilling muds, etc.
35-37	Methacrylic cid (60), Ethylacrylate (40)	Divinyl benzene (0.1) or N-methylol acrylamide	-	Uncross linked polymer used for printing with C.I. Red dye. Cross linked polymer for pigment printing (Partial substitution of Kerosene).
38-42	Methacrylic acid (55-65),	EGDMA or N,N-methylene bis acrylamide (2-	Initiator: alkali metal persulfate, anionic	Used for printing of cotton with pigment , reactive

	Butyl acrylate (35-45)	17%)	emulsifier.	and metal complex dyes.
43	Acrylic acid (2.9), Styrene (4.0), Butyl acrylate (14.0), Ethyl acrylate (10.0), Sodium styrene sulfonate (0.4) Polyoxyethyl nonyl phenyl ether (0.3)	N-Methylol acrylamide (1.2)	Initiator : ammonium persulfate, 0.2% sodium metabisulfite water: 13.5 parts, 45^{0}C.	Mn≥ 500,000, used for pigment printing.
44	Methacrylic acid (168), Butylacrylate (15), Ethyl acrylate (5)	Butanediol diacrylate (2)	-	Used for printing cotton with Ryu dye w.
45	Methacrylic acid (45), Methyl acrylate (42), Methyl methacrylate (5)	EGDMA (8)	-	Average grain size 640 A^0. shear thinning property.
46	Iso-butyl vinyl ether (200) Di-ethyl maleate (172)	-	Peroxy ester initiated polymerization, 60-80^{0}C	Used in textile printing pastes, cosmetics, pharmaceuticals.
47	Maleic anhydride (98) Methacrylic acid (1 Part) Ethyl acrylate (99 Part)	-	Water (574g), Abex zzs anionic surfactant (11.2g), gel pol CO 497, CO 997. Nonionic sufactant (1.7g), $K_2S_2O_8$ (0.13g) at 180^0 C in the presence of a metal oxide.	Used as textile adhesive coatings and viscosity enhancers.

Table 1.2(d) Inverse Emulsion Polymerization

Refs.	Monomer(s) (Parts)	Crosslinking monomer	Polymerization conditions	Properties / uses
48	Acrylic acid (200) Acrylamide (25)	1% methylene bisacrylamide (15.8)	Initiator : 2,2'azobis (2-amidio propane) - 2HCl (0.112g); Hydrocarbons: 250g, Water : 288g.	Average particle size 4 µm. Used for pigment printing on 65: 35 PET/Cotton.
49	Acrylic Acid	Polyallyl ether of sucrose with 5 to 8 allyl gps (0.5-2%)	Cationic surfactant in mixture of organic solvents	In textile printing.
50	Acrylic acid (68.4) Acrylamide (3.55)	Bisacrylamido acetic acid (0.00331g)	Water (113g) mixed with mineral oil, Emulisifier (3.7%) of HLB value more than 7.	Used for pigment printing.
51	Acrylic acid (83) Acrylonitrile (58) Acrylamid (12)	1% Methylene bisacryl-amide (2.8g)	Water (127g), Paraffin oil (47g), n-octane (145g), emulsifier: sorbitan monoleate (10.5g), Initiator : t-butyl peroxide, 40-50^{0}C, 3 hours, pH = 6.5.	Used for printing of PET - cotton with alizarin Blue RT.
52	Acrylic acid (158g)	Pentaerythritol triallylether (1.36g)	Presence of diacetyl peroxy carbonate in a 70/30 $CH_2 Cl_2$ /EtOAc. Mix. at 35^{0}C.	Used as thickening agent.
53	Acrylamide (60	-	Organic medium	Viscosity = 3500

	parts), Acrylic acid (200 parts)		(aliphatic hydrocarbons) , SPAN 80 (25 Parts), EDTA Sodium salt (1925 ppm), 2-2 bis acrylamide (539 ppm) and Sodium chlorate (3846 ppm)	cP. (VKRV 8 Viscometer, spindle - 3,20 rpm) at 25^{0}C.
54	Acrylic acid (80%) (172g) Acrylamide (50%) (66g)	Dimethylene triamine pentaacetic acid (1.1g)	Solvent : toluene (213g), 70^{0}C temp, Initiator : Sodium metabisulphite, In presence of surfactants in water (160 g)	Used as flocullent and as textile print paste thickener.

1.3.1 Solution and Precipitation Polymerization

These two types of polymerizations are the polymerizations carried out in the presence of a solvent for the monomer. The solvent may also be a solvent for the polymer as well. If it is, then the end product of the reaction is a solution of polymer in solvent, if it is not, then the polymer precipitates from the system as it forms and the result is a slurry of polymer. In the former system, known as solution polymerization, the polymerization system will remain fluid over the whole course of the reaction, if sufficient solvent is present. In the latter system, known as precipitation polymerization, the reaction system is, in part atleast, heterogeneous [55].

Many patents disclosed the use of solvents like toluene [33], benzene [24], ethyl acetate [27] and cyclohexane [25] etc. Dimethylaminopropyl methacrylamide and N-N'-dimethyacrylamide along with

polyethylene glycol dimethacrylate have been polymerized using water as a solvent [29].

The presence of solvent serves a number of functions as it reduces the viscosity of the reaction mass allowing effective agitation and acts as a heat sink for the heat of reaction. Also when polymerization is carried out at the reflex temperature of the solvent, the 'latent heat of vaporization' of the boiling solvent will effectively remove excess heat from the reaction mass and will act to maintain the temperature at the reflex temperature of the solvent.

The molecular weight distribution is effected by the precise method employed to prepare the polymer. Two techniques used commercially are [56]:

1. All in process (or one shot process).
2. Drip feed process (or continuous process).

The **'All in Process'** involves charging all the monomer, solvent, initiator and modifier into the reaction vessel and heating to reaction temperature. As the initiation and propagation occurs, the temperature of the reactants is allowed to rise to the reflux temperature of the solvent present. The reactants are held at reflux temperature under total reflux conditions, to condense all vapours and return the liquid to the reaction vessel. The latent heat of vaporization of solvent and monomers helps to dissipate the heat of reaction. A wide molecular weight distribution may result from this type of process.

The **'Drip-feed process'** involves feeding of monomer and initiator, separately, into solvent at reaction temperature. Ideally, as the monomer and initiator come into contact with the hot solvent, free radicals are

formed which immediately initiate polymerization of the monomer. At any time during the polymerization, the relative amounts of monomer, initiator, modifier and solvent are all reasonably constant. This favours the formation of polymers with a narrow molecular weight distribution.

By controlling the relative rates of the monomer and the initiator feeds, it is possible to influence the molecular weight and molecular weight distribution. This is known as 'starved feed' techniques. The use of drip feed process allows more lattitude in the preparation of constant composition copolymers.

1.3.1.1 Factors Influencing Polymerization

There are various factors influencing polymerization [56] as given below:

a. Reaction temperature
b. Monomer concentration
c. Solvent
d. Concentration of Initiator
e. Chain transfer agents
f. Tromsdorf effect.

a. Reaction Temperature

Generally the molecular weight of the polymer decreases with increasing temperature of the reaction. More initiator molecules are decomposed per unit of time as the temperature is increased. Thus there are more radicals available at any given time and hence more chains are initiated in the presence of the same number of monomer molecules, thus reducing the number of monomer units incorporated perchain. The result is a lower molecular weight polymer and, for a given solvent a lower solution viscosity. Close control of temperature is therefore essential to ensure consistent molecular weights.

b. Monomer Concentration

Molecular weight is influenced by the monomer concentration. Usually the lower the concentration of monomers the lower the molecular weight of the polymer formed. High concentration of monomer generate a greater chance that the monomers will come into contact with a propagating chain, and therefore reducing the possibility of chain termination by the solvent or any other chain terminating species which may be present. Hence the resulting polymer will have a higher molecular weight and higher viscosity.

c. Solvent

Not only does the choice of solvent influence the solution viscosity, but the different degrees of chain transfer activity associated with different solvents affects the molecular weight of the polymer formed. The initiator half life being affected by certain solvents. The boiling point of the solvent has a major influence on the reaction conditions since its presence during the polymerization dictates the maximum reaction temperature which can be utilised. In turn the reaction temperature will influence the choice and quantities of initiator and modifier used to achieve the desired molecular weight and degree of conversion. Thus solvent combinations are often used to allow the polymerization to be carried out at a suitable reaction temperature.

d. Concentration of Initiator

Commercial polymerizations usually employ between 0.2-4% of initiator. When the concentration of initiator is reduced , the molecular weight of the polymer is increased, but the conversion of monomer to polymer is reduced. Higher concentration of initiator form a greater

number of polymer chains. These chains are shorter and hence molecular weight and viscosity are lower.

The most commonly used technique for generating free radicals is that of the thermal decomposition of a peroxide orazo compound. Some commonly used initiators with their half lives ($t_{½}$) at various temperatures are given in Table 1.3.

Table 1.3: Commonly Used Initiators and Their Half Lives at Various Temperatures

S.No.	Initiator	Temperature (^{0}C)	Half life ($T_{½}$)
1	Dicumyl peroxide	100	20 hr.
		120	5.5 hr.
		130	2.0 hr.
		140	35 min.
		150	12 min.
		160	4.5 min.
2	Di-tertiary butyl peroxide	130	6 hr.
		140	2 hr.
		150	40 min.
		160	15 min.
3	Dibenzoyl peroxide	80	4hr.
		90	1.25 hr.
		100	25 min.
		110	8.5 min.
4	Azo bis-isobutyronitrile (Also known as azodi isobutyro nitrile)	64	10 hr.
		82	1 hr
		100	6 min.
		120	1 min.

However half life for any given initiator does not only depend upon the reaction temperature, but also upon the reaction environment and the concentration of initiator present. Azo initiators such as 2-2' azobis isobutyronitrile (AIBN) do not cause the oxidation effects which can occur with peroxy compounds, particularly where labile hydrogen atoms are present (e.g. acrylate monomers).

e. Chain Transfer Agents

A chain transfer agent terminates a propagating chain, whilst making the free radical available to initiate the propagation of another chain. The higher the concentration of the chain transfer agent, the lower the molecular weight and hence, the lower the solution viscosity for a given solvent. So a careful selection of the solvent is required.

The effect of different solvents has been studied in the acrylic acid (AA) and pentaerythritol tetrallyl ether polymerization [25]. 58.54 parts maleic anhydride and 50.5 parts isobutylene copolymer cross linked with 14.2 parts n-docosyl methacrylate has been polymerized by solution polymerization using ethyl acetate and isopropanol mixture as a solvent and AIBN as the initiator [26].

f. Tromsdorf Effect

This effect occurs within system when there are un-reacted monomer molecules in solution. As polymerization proceeds, the solution becomes progressively more and more viscous and the movement of all molecules is reduced, with the large molecules being most affected. Under these circumstances propagating radicals can no longer freely contact each other and the rate of termination is greatly reduced. The number of radicals increases and the rate of reaction increases correspondingly. At

the same time, the half time of the propagating radical is increased as a result of which the molecular weight of the polymer increases rapidly. The 'Tromsdorf Effect' is important in all commercial polymerizations, where a high degree of conversion is required. It is most marked in systems containing methyl methacrylate.

1.3.2 Emulsion Polymerization

Emulsion polymerization is one of the most important technique of polymerization in heterogeneous system and consists of two immiscible liquid phases, an aqueous continuous phase and a non-aqueous discontinuous phase. The external or aqueous phase consists of water, salts, buffers, initiators and emulsifiers. The internal phase initially contains micelles containing monomer and monomer droplets. The basic components in emulsion polymerization are:

1. Monomer
2. Water
3. Surfactants
4. Initiator
5. Protective Colloids
6. Buffers

Besides these components sometimes a chain transfer agent is used to control the molecular weight of the polymer formed.

Copolymers of hydrophilic monomers like acrylic acid, methacrylic acid, and itaconic acid and of hydrophobic monomers like esters of methacrylic acid, styrene are the products of commercial interest due to their wide applications. By using emulsion polymerization process, polymers having higher molecular weight can be obtained from the reaction medium having relatively low viscosity.

The polymerization of hydrophilic and hydrophobic monomer system is not truly emulsion polymerization. The polymerization occurs in water

phase as well as in micelle phase. A two loci polymerization mechanism [57]. As one of the monomer to be used in a water soluble acrylic acid or methacrylic acid, the course of mechanism of polymerization is different from the conventional emulsion polymerization.

Consideration will be given to the differences [58] in the polymerization of hydrobhobic and hydrophilic monomers (table 1.4).

Table 1.4: Emulsion Polymerization in the Presence of Emulsifier

S.No.	Parameter	Hydrophobic Monomer	Hydrophilic Monomer
1.	Locus of Initiation	Micelle	Micelle and water phase large
2.	Amount of Emulsifier	Small	Large
3.	Distribution of emulsifier	Surface of particles	Surface and inside of particles.
4.	Particle Size	Small	Large
5.	Stabilization of particles	Easy	Difficult
6.	Degree of polymerization	High	A little high
7.	Film forming ability	Poor	Good
8.	Water resistance of polymer	Good	Poor
9.	Use of Protective colloid	Un-necessary	Necessary

It was reported that in soapless emulsion polymerization of methyl methacrylate (MMA) and Butyl acrylate (BA), introduction of methacrylic acid (MAA) imparts heterogeneity in copolymer composition, which is reflected by multiple glass transition temperature [59]. In the polymerization of MMA, BA and MAA an increase in MAA content increases the particle size and viscosity, while stability of emulsion is reduced [60].

As compared with diene emulsion polymerization, systems for acrylates require higher reaction temperatures, less reaction time, less initiator, a pH of 7 or lower and the use of synthetic micelle generators rather than of soaps from natural sources. Control of pH is important in order to prevent hydrolysis of the monomer. Emulsion polymerization carried out in media of high pH is accompanied by some saponification of monomer, whereas hydrolysis is negligible if the pH is 7 or lower [55].

In emulsion polymerization, the generation of micelles and also the stability of the polymer emulsion are markedly influenced by the quality of water used. The presence of polyvalent metal ions may inhibit the polymerization reaction and may cause flocculation of the polymer emulsion. Univalent ions in higher levels also influence the formation of the micelles and adsorption of the stabilizing surfactants on water. Therefore de-ionised water is preferred for the process of emulsion polymerization, because in de -ionized water salt content is extremely low, which permits the maximum control on the composition of the emulsion.

The surfactants controls may of the properties of emulsion polymers and some knowledge of their nature and characteristics is a necessary prerequisite for successful formulation of latex system. Any molecule containing a hydrophilic group chemically bound to a hydrophobic group

can act as a surfactant. When a surfactant is dissolved in a water/oil mixture, the individual molecules concentrate at the water/ oil interface where the hydrophilic groups are in the water phase and the hydrophilic groups are oriented towards the oil phase. The surface tension of the system is essentially that of the hydrophobic group. The concentration of individual surfactant molecules in water is limited. There is a critical concentration below which a surfactant will not form micelles. The minimum level required for micelle formation is known as the critical micelle concentration (CMC), and varies with surfactant types. The surfactants can be anionic (alkali salts of fatty acids and of aryl and alkyl sulfonic acids), cationic (alkyl amine hydrochlorides and alkyl ammonium halides) or non-ionic (alkyl glycosides and saccharose esters fatty acids [61].

The requirements of emulsifier for emulsion polymerization are for good emulsion stability and faster conversion rate. The HLB value of an emulsifier decides its suitability for different systems [62]. For oil-in-water system HLB value between 8-15 has been found suitable.

The initiators used in emulsion polymerization are exclusively of free radical type and of necessity, they must be water soluble. The major initiator used in commercial emulsion polymerization are persulphates of sodium, ammonium and potassium. When per sulphates are involved, the major initiating species is the sulphate ion radical.

In the emulsion system, as the polymerization process proceeds, the density of the system increases which is a process of destabilization. As the density increases the polymer formed tends to coalesce, thereby leading to the separation of the polymer emulsion i.e. de-emulsification. A protective colloid is thus used in the system to increase the viscosity of the

medium and to prevent the separation of the polymer form the water phase i.e. to stabilize the emulsion. Examples of protective colloids are polyvinyl alcohol, gum arabic, gum traga canth and derivatives of natural products, such as hydroxy ethyl cellulose and starch ethers. Hydroxy ethyl cellulose is used with pure acrylic emulsion but normally more sophisiticated polymerization techniques are required.

In emulsion system buffers are often added to stabilise the pH of the reaction mass. The presence of persulphate initiator leads to acidic residues being formed in the process which may considerably lower the pH of the system. To prevent a large drop in pH, the system would normally be buffered at about pH 5.0. The reasons for the need of buffers are as follows:

1. Some surfactants are pH sensitive with regard to micelle formation and latex stability.
2. Some initiators are pH sensitive.
3. Copolymerization may occur better at a specific pH e.g., acrylic acid & methacrylic acid do not form copolymers easily above pH 5.
4. Some monomers may be hydrolyzed at alkaline pH.

Typical buffers employed are borax, sodium hydrogen phosphate, sodium bicarbonate and sodium acetate etc.

1.3.3 Other Polymerization Techniques

Other polymerization techniques for the synthesis of synthetic thickener include inverse emulsion, suspension, and radiation - induced polymerization techniques.

In inverse emulsion technique polymerization is done in the presence of a water-in-oil emulsifier. The inverse emulsion polymerization process yields a viscous latex consisting of hydrophilic polymer particles swollen by water in the continuous phase [63]. Effect of polymerization conditions such as initiator concentration, monomer, cross linking agent, pH and polymerization temperature etc. on thickening property of polyacrylic acid latex has been studied. Latex having good electrolyte resistance can be obtained by polymerization with non-ionic hydrophobic commoners such as acrylamide at selected pH [64].

Heat sensitive thickeners have been prepared [65] by inverse emulsion polymerization technique from N-isopropyl acrylamide with methylene bis acrylamide as cross linking agent in the present of hydrophobic emulsifier sorbiton monooleate in hexane. For the preparation of thickener by inverse emulsion technique, hydrophilic monomers like ethylenically unsaturated acids, amides are employed [52-54]. Sodium acrylate has also been successfully polymerized in a water-in-oil emulsion with polyoxyethylene glycol diglycidyl ether as the cross llinker [66]. The amount of emulsifier required to obtain a stable emulsion in these systems is very high (3-7% based on the weight of monomer).

In suspension and in reverse suspension polymerization, every dispersed monomer droplet acts as a tiny bulk reactor. These droplets are very active for agglomeration. Suspending agents, stirrer speed and design of stirrer play an important role in preventing agglomeration.

The synthesis of cross linked acrylic acid polymer using the radiation induced inverse emulsion polymerization techniques with Kerosene as the oil phase has been reported [67]. The emulsion can be

directly converted into a printing paste, hence eliminating the effect of initiators on the final print.

1.4 COPOLYMERIZATION AND REACTIVITY RATIOS

1.4.1 Copolymerization

In copolymerization, two or more monomers/ monomer pairs are polymerized simultaneously and hence, the polymer is composed of more than one repeat unit. In general, copolymerization can be represented as

XA + yB → -A-A-B-A-A-A-B-B-B-B-A-B-A-B-B-

The copolymer formed is composed of both the monomeric units A and B arranged at random. The A:B ratio and the degree of randomness depend on the quanity of the individual monomers taken, their ameniability for copolymerization and the polymerization mechanism used [61]. The majority of the commercially import copolymers are made by free radical ionic or polycondensation polymnerization.

1.4.2 Reactivity Ratios and Copolymerization Behaviour

The ratio r_i can be considered as the tendency of monomer M_i to react with itself or to react with another monomer type present (i.e. to form a copolymer). The value of r_1 and r_2 indicates the composition and structural type (i.e. random or block) of the copolymer being produced. Depending on the values of r_1 and r_2 various copolymerization behaviours (56, 61) are possible some of which are discussed below:

(a) When $r_1 = r_2 = 0$, In this case, a chain ending with M_1 will add only an M_2 and this M_2 will add only at M_1, which inturn, will add only on M_2 and so on. The copolymer formed will have on equal number of M_1 and M_2 monomeric units arranged alternatively in the copolymer chain formed. We thus get a strictly alternating copolymer,

irrespective of the monomer feed ratio. It may be interesting

irrespective of the monomer feed ratio. It may be interesting to note that the individual monomer falling under this category can not form homopolymers, but when polymerized together, can form an alternating copolymer.

(b) When $r_1 = r_2 = 1$. In this case, all the four types of propagation reactions are equally possible. Both ~ M_1 and ~ M_2 radical types show a similar preference for adding M_1 and M_2 monomer units. In this case the resulting copolymer will be of random distribution and the copolymer composition will directly reflect the starting monomer composition. This case can be called an 'Ideal Copolymerization', since the copolymer composition can be ideally controlled by adjusting the initial monomer feed ratio. Since the feed compositions and the copolymer composition remain constant throughout the course of the polymerization, this type of copolymerization is also called the 'azeotropic copolymerization'.

(c) When $r_1 > 1$, it indicates that the propagating species will only add to its own monomer unit. This will result in homopolymerization particuarly if r_2 approaches to zero.

(d) When $r_1 > 1$, it indicates that the propagating species prefers to add to monomer unit of the other species. This result, in generation of alternating copolymer.

(e) When $r_1 > 1$ and $r_2 > 1$, such a system does not usually undergo random copolymerization. It form either a mixture of the two homopolymers or, under certain favourable conditions, block copolymers having long sequences of M_1 followed by a long sequence of M_2.

(f) When $r_1 < 1$ and $r_2 < 1$. In this case, M_2 and add on to M_1 and M_1 can add on to M_2. The preference for one of these two will depend on the actual values of r_1 and r_2 and also on the monomer feed ratios.

The reactivity ratios are essentially independent of temperature, solvent and other factors which have an effect on the overall reaction rate.

1.5 RHEOLOGICAL PROPERTIES OF SYNTHETIC THICKENERS

1.5.1 Viscosity Development

Knowledge of viscosity development is of fundamental importance for synthetic thickeners used in pigment printing. Acrylic based thickeners contain commoners having carboxylic acid groups. The polymer chains are randomly coiled in acidic pH and their average end to end distance is low. Viscosity develops immediately after the addition of a base by the neutralization of carboxylic groups. Repulsion of like cationic and anionic charges then cause uncoiling of the molecule into an extended structure. This leads to increase in viscosity [15].

Inorganic bases such as sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonium hydroxide (NH_4OH) and sodium bicarbonate ($NaHCO_3$) and organic bases such as low moleculear weight alkanol amines and alkyl amines have been used for neturalization of synthetic thickener. Ammonium hydroxide is the most commonly used base for the neutralization of synthetic thickeners, because it evaporates during the process of curing and provide the acidic conditions which are necessary for the correct cross linking of the binder.

Brookfield RVT viscometer is convenient for measurement of viscosity at low shear rates. It measures the torque required to rotate a spindle through a sample at 0.5 to 100 rpm. Multiplying the torque dial

reading by a constant (depending upon the spindle size and speed) gives apparent viscosity of the sample. Increasing the speed results in a corresponding increase in shear rate. In this way flow properties can be examined by observing torque as spindle speed is varied.

1.5.2 Various Factors Affecting Viscosity

The viscosity development of synthetic thickeners depends on various parameters as discussed below:

a.	Copolymer composition	b.	pH
c.	Shear rate	d.	Crosslinking density
e.	Electrolytes concentration.		

a. Effect of Copolymes Composition on Viscosity

Viscosity of synthetic thickener depends upon the amount of carboxylate ions. Brookfield viscosity of methacrylic acid and ethyl acrylate (MAA/EA) copolymer, on neutralization with ammonium hydroxide, increases with methacrylic acid fraction in the copolymer, but after certain value, viscosity decreases with the increase in methacrylic acid (MAA) fraction [68]. This is attributed due to increase in glass transition temperature of the copolymer with the increasing of MAA fraction and decreasing of EA fraction in the copolymer. Ethyl acrylate lower the glass transition temperature of the copolymer and hence, indirectly contributes to the development of viscosity. It is necessary to optimize the comonomer fraction for the development of high viscosity in low amount of synthetic thickener.

b Effect of pH on viscosity

Viscosity of the synthetic thickener is pH dependent. When ammonium hydroxide (NH_4OH) is added to polymer emulsion in water. Some ionization occurs providing NH_4+ ions, some ionization occurs providing NH_4+ counter ions. After complete neutralization, further addition of ammonium hydroxide result in build up of NH_4^+ counter ions. As the polymer chains contains carboxylate (COO^-) ions, formation of ammonium counter ions leads to decrease in ionization of COOH group by the effect of law of mass action and the common ion effect and hence the extended chains start recoiling and viscosity falls.

The optimum pH for working with a pigment printing paste ranges between 8 and 9. It is not advisable to exceed pH 9. This will cause the lowering of the viscosity of the paste. It is also not advisable to work at a pH lower than 8, since this may cause, during the printing phase, the beginning of the cross linking of the binder - specially when using a fixing agent (also called fixer) and will result into the clogging of the Screens [14].

c. Effect of Shear Rate on Viscosity

In Newtonian systems flow is directly proportional to applied stress i.e., no loss in viscosity as shear rate increases. Pseudoplastic solutions flow more readily as shear rate is increased. Solutions exhibiting plastic flow do not flow until the applied stress exceeds a certain minimum value, which is called yield value. The yield value provides stability to emulsions and suspensions.

Synthetic thickeners are pseudoplastic. Their viscosity decreases with an increase in shear rate, which is the necessary requirement for a printing paste. In an US patent [69], Brookfield viscosity (at 20^0C) of an acrylic

based synthetic thickener are claimed to be 1,36,000 cPs, 17,000 cPs and 4,400 cPs at spindle speed of 0.5, 10 and 100 rpm respectively.

According to Kullicke, Kriewske et al the observed drop in viscosity values with increase in the shear rate may be related to the break down of the hydrate or solvent enveloped network chains of polymer in the dispersion, by mechanical action. Mechanical stress separates loosely linked polymer chains, results in decrease of viscosity [70].

d. Effect of Cross Linking Density on Viscosity

The small degree of transverse cross linking bind the polymer chain together. In the acidic state, polymer chains remains in normal coiled form. On neutralization with a base, the chains become polyanion and under the action of strong repulsive force straightening and separation of chain occurs to a maximum possible extent. Because of cross linking they act as hydrated particles with more than hundred fold expansion of its original size but are held in a tightly packed condition. This change results in a very high viscosity of the paste.

The more is the cross linking density, the more is the gel content and more is the viscosity of neutralized synthetic thickener. Brookfield viscosity increased linearly with gel content was observed for methacrylic acid and ethyl acrylate copolymers with ethylene glycol dimethacrylate (EGDMA) and N-N' methylene bisacrylamide as cross linking agents [68].

In loosely cross linked polymers, a printable viscosity can be accomplished at a much lower solid content compared to linear copolymers. This is of great importance because a low solid content enhanced the feel of a fabric as well as its wash fastness properties.

e. Effect of Electrolyte Concentration on Viscosity

Electrolyte insentivity of the polymeric thickener is very much desirable from the usage point of view. A drop in viscosity observed when ions are added in the form of a salt e.g ammonium sulphate, sodium chloride etc. [71]. The electrolytes or salts which are added externally decrease dissociation by common ion effect resulting in the drop of viscosity.

Brookfield viscosity (at 20^0C and 20 rpm) of printing paste containing acrylic thickener reduced from 25,000 cPs to 15,000 cPs upon addition of 0.1% sodium sulphate (Na_2SO_4) solution [72]. In case of uncrosslinked polymers, though the polymeric chains are recoiled, but they remain in the dissolved state, so the drop in viscosity is not as high as in case of cross linked polymers.

A drop in viscosity on adding of electrolytes is the major disadvantage of synthetic thickeners. It makes them less suitable for printing with dye formulations containing salts. Pigment dispersion manufacturers are now serious about its electrolyte content. One such pigment dispersion system with nonionic surfactant is claimed to retain the viscosity of highly electrolyte sensitive thickener with it even at high concentration of pigment [73].

1.6 PERFORMANCE OF ACRYLIC THICKENERS

Conventionally, Kerosene emulsion is used as a thickener in pigment printing. Pigments prints on cotton fabric using Kerosene emulsion in water are characterised by good colour fastness and high degree of brilliance with soft hand. However there is an increasing tendency towards the substitution of Kerosene by synthetic thickeners due to various disadvantages like risk of explosion in the driver, air and water pollution,

loss of valuable Kerosene during drying and curing processes and inadequate availability of Kerosene for domestic use. Successful use of an aqueous system for pigment printing and its beneficial effect on safety environment pollution and economy of operation has given impetus to the use of synthetic thickeners. One more advantage of synthetic thickeners is that, no external catalyst is required for fixation as the carboxylic groups present in the polymer chain are sufficient to activate the fixation reaction [74].

It is believed that during fixation reaction, the functional groups of the binder react with the hydroxyl groups of cellulose i.e. of cotton and fixer (e.g. methylol melamine) form a film on the surface of the printed cloth. For the fixation reaction, acidic pH is required.

Binder -CH_2OH + HO-Cellulose

$\downarrow$ (pH=3)

Binder - CH_2-O-Cellulose + H_2O

It was assumed that the ammonium carboxylate groups formed by the neutralization of the acid groups during the preparation of paste liberate ammonia (NH_3) during the process of curing and acid groups and regenerated giving the pH on acidic.

Catalyst in pigment printing is used to accelerate the cross linking of binder molecules and facilitate the reactions between the reactive groups like N-methylol acrylamide and hydroxyl groups. This occurs at acidic pH. In case of Kerosene emulsion, diammonium hydrogen phosphate (DAP) is added as a catalyst. At curing temperature (150^0C), diammonium hydrogen phosphate (DAP) generates phosphoric acid (H_3PO_4) and

ammonia (NH_3). Ammonia goes away and phosphoric acid provides the required pH of 3.

$$(NH_4)_2HPO_4 \xrightarrow{150^0C} H_3PO_4 + 2NH_3^-$$

The major characteristics which should be considered when evaluating the performance of a synthetic thickeners are printability, colour yield, simplicity to use, stability, softness and viscosity yield. The thickener should into negatively influence, the color yield of the pigments being used and the brightness of the shade. A good thickener must provide for good levelness of the prints. The use of thickener should give an homogeneous printing paste within reasonable time. The thickener must have a good storage stability and not separate out. The thickener must have a minor influence on the hand of the prints and should also provide a suitable viscosity at low concentration [14].

The performance of acrylic based synthetic thickener [13] has been evaluated in comparison with prints obtained from Kerosene emulsion thickener on cotton fabric The prints were taken with red, blue, yellow and black pigments. The colour value was found lower than Kerosene emulsion. Dry and wet rub fastness properties were comparable with Kerosene emulsion when cured for 5 minutes at 170°C. Bending length was found 2.5-2.58 cm. in comparison to 1.6-1.67cm. for Kerosene emulsion. However by using 80:20 and 60:40 (weight / weight) blends of synthetic thickener and Kerosene emulsion, the handle of the printed cloth improved significantly.

Bhagwat et. al. has also carried out the pigment printing of hosiery goods using synthetic thickeners [3] system. A ready to use Khadi printing formulation was prepared using synthetic thickener as a base material.

The fabric oriented with this formulation could with stand carbonisation treatment and could retain good level of fastness.

A Japanese patent reveals the use and performance of methacrylic acid, ethyl acrylate and butyl acrylate polymer cross linked with butanediol acrylate in a printed cotton fabric with 5 percent Ryu dye W Turquoise Blue FB [44]. The printed fabric was cured for 3 minutes at 150^0C temperature. The prints obtained had good fastness to colour and handle.

M.N. Chapatwala and Mantra reported the hardening and browning of thickener [75]. Stiff prints are generally a result of hardened thickeners which could not be removed in washing. The degree of hardening may depend on the efficiency of the washing equipment and procedure (such as reduction clearing). Browning of a thickener can be clearly seen when bright pale shades are impossible to achieve or better when the thickener system together with all the chemicals are printed without a dyestuff present. Hardening and browning problems are more common in high temperature ageing and hot air fixation. Browning is more severe in high temperature ageing, whereas hardening is more pronounced in hot air fixation. Both are increased by longer times and high temperatures. The type and amount of acid used in pH adjustment of the print paste is an important consideration, since a low pH tends to increase both browning and hardening. It should be noted that reduction clearing deters both browning and hardening. Alginates and synthetic thickeners, in general, do not exhibit browning and hardening.

In the field of pigment printing many a times, it is suspected that the thickeners as such does not cause stiffness to the prints, but only product interaction of thickener and binder control the handle of fabric, since most of the binders are acrylic based binders. In the absence of binder, the

study revealed a slight improvement in the feel of the fabric but the wash fastness was poor indicating an incomplete fixation of the pigment. Hence it was emphasized that a separate binder is necessary with synthetic thickeners [76]. However, the use of some softeners may improve the handle of the prints. A considerable amount of work has also been carried out with disperse and reactive dyes on PET-cotton blends and cotton fabric using polyacrylamide thickeners [77]. The colour value comparable but the feel of the fabric was inferior. Saponified polyacrylonitile based on acrylonitrile and acrylic acid copolymers has also been used for the printing of cotton fabric with vat and reactive dyes. The colour value was higher than the alginate printed samples and had equally good fastness property. The feel of the fabric was soft.

Methacrylic acid, butylacrylate compositions in a loose three dimensional network using EGDMA or N-N-methylene bisacrylamide as the cross linking agent have found effective use in pigment print paste formulation [38-42]. MAA/ EA/DVB/N-methylol acrylamide polymer has lso been used with pigments for partial replacement of Kerosene.

MAA/BA/MMA terpolymers have been used in pigment printing for partial substitution of Kerosene These terpolymers have good resistance toward electrolytes. For partial substitution of Kerosene in pigment printing, A polymmer of acrylic acid, ethyl acrylate, butyl acrylate and styrene cross linked with N-methylol acrylamide has been used successfully to obtain stable prints on cotton / polyester fabric. Acrylic acid has been more commonly used in the form of acrylic acid / acrylamide copolymer. Acrylic acid-acrylamide copolymers of varying concentration of two monomers and different cross linking agents have been used to replace Kerosene in pigment printing. Methyl methacrylate polymers are also used as

thickeners [20] and fabric printed with them have good handle, wash fastness and colour yield.

Different systems have been evolved replacing Kerosene completely or partially and are being used commercially. The commercial acrylic based synthetic thickeners being used in India are Alcoprint (Allied colloids), Lutexal HEF (BASF India Ltd), RAN - 5000 (RSA Polymers) and carbopol (B.F. Goodrich) etc. Alcoprint PTG and PTU are neutralized grades of Alcoprint PTF. These grades do not need the addition of ammonia. Alcoprint PTH is a modified polyacrylic thickener which overcomes the problems associated with the black pigment (such as problem of gelling). Alcoprint 7860 is the anionic polyacrylate dispersion with good electrolyte stability and storage stability for use in reactive and disperse dye printing system. It is relatively insensitive to dyestuff adding and can be used as a stock thickening. Alcoprint 7860 is particularly suitable for printing all types of polyester fabric with disperse colours.

Lutexal thickeners of various grades are available. Lutexal HEF is reported to be suitable for use in both aqueous and emulsion pigment printing system, but only a slight influence on the handle of the prints. It is claimed that print pastes based on Lutexal HEF have excellent running properties and produce brilliant prints with sharp outlines.

RAN - 5000 is polymer thickener available as a pourable liquid, anionic in nature and can be successfully substituted for emulsion printing. RAN - 5000 can eliminate Kerosene completely or partially depending on the needs of the printer.

Carbopol thickeners of various grades are available. These have many other applications besides in textiles printing paste. Carbopol resins are acrylic acid polymers in the form of fluffy dry powder Carbopol 846 is

very high efficient synthetic thickener used for pigment printing. Carbopol 934 P is especially for the pharmaceutical industry, while Carbopol 940 is for cosmetic applications.

CHAPTER - 2

SYNTHESIS AND CHARACTERIZATION OF MAA - EA COPOLYMERS CROSS LINKED WITH ALLYL METHACRYLATE (AMA)

2.1 INTRODUCTION

Methacrylic acid - Ethylacrylate based synthetic thickeners are the products of commercial interest for last two decades for replacement of Kerosene in pigment printing. Two types of polymerization reactions, namely emulsion and solution polymerization, are mainly carried out for the synthesis of polymer for synthetic thickener. Polymerization of hydrophilic monomer (e.g. methacrylic acid) and hydrophobic monomer (e.g. ethyl acylate) is not expected to follow true emulsion polymeriation mechanism. This is ascertained based on partition of MAA in the aqueous phase and organic phase. In solution polymerization organic solvents (single or suitable mixture) in which the monomers are soluble are used as a medium for polymerization. Polymer after its synthesis becomes insoluble in solvent and remains as suspension at the end of polymerization unlike conventional solution polymerization. The suspended polymers are separated by filtration / evaporation of the solvent as fine solid powder.

2.2 SOLUTION POLYMERIZATION

In solution polymerization, the molecular weight of the polymer is regulated by the chain transfer constant of the solvent, so a careful selection of the solvent is required to minimize this effect and achieve a polymer of sufficiently high molecular weight. Various solvents like benzene, toluene, ethyl acetate and cycohexane-methyl isobutyl ketone have been used for the polymerization of acrylic acid / alkyl acrylate. From the literature survey, it is evident that acrylic polymers containing MAA as the major comonomer are used as synthetic thickeners in textile printing.

In the present study, the polymerization of MAA-EA using the solution polymerization technique is reported. Allyl methacrylate (AMA) is used as the cross linking agents. Copolymers obtained at high conversions were characterized using acidimetry and infrared spectra.

2.3 EXPERIMENTAL

2.3.1 Materials

Methacrylic acid (MAA) and ethyl acrylate (EA) (Provided by Vam Organic Chemicals Ltd.) were used as comonomers. Allyl methacrylate (AMA) (MERCK - Schuchardt) was used as cross linking agent and 2-2' azobisisobutyronitrile (AIBN) (High Polymer Labs) was used as initiator. Toluene (also provided by VOCL) was used as a solvent.

2.3.2 Polymer Synthesis

MAA-EA copolymers of varying compositions (MAA 50-70 wt%, EA 30-50 wt%) were synthesized by using solution polymerization technique. The solvent used was toluene. Allyl methacrylate (AMA) with varying amount of 0.75 to 1.75 wt% of total monomer was used as cross linking agents. 2-2' Azobis isobutyro nitrile (AIBN) (also known as AZDN) with 0.15 wt% of monomer was used as free radical initiator. The recipe of 1000g batch is given in Table 2.1.

Table 2.1 Polymerization Recipe

Compound	Weight (g)
Methacrylic acid (MAA)	100-140
Ethyl acrylate (EA)	60-100
Allyl methacrylate (AMA)	1.5 - 3.5
AIBN (Initiator)	0.30
Toluene	800

Time : 5 hrs, Temperature : 111^0 C, Toluene : Monomer :: 4:1

First of all 800 g toluene was taken in a 2 litre glass reactor. The glass reactor was equipped with mechanical stirrer (with a facility to vary the speed of stirrer), a thermometer (for control of temperature), a reflux condensor and a dropping funnel (for initiator feedings). Monomer (MAA and EA) were mixed with chosen quantity of allyl methacrylate. 150g of this mixer was added to the refluxing toluene while being stirred.

In the rest of monomers and AMA solution, 0.30 g AIBN was mixed. Feeding of this monomer solution and initiator (AIBN) was done to the refluxing toluene in 3 hours. The stirrer speed was kept at 120 rpm. The temperature of the glass reactor was maintained at 110-111^{0}C (i.e. refluxing temperature of toluene). A holding time of 2 hours was provided so that maximum conversion of monomers to polymer formation took place.

The medium of solvent was such that the polymer after its synthesis becomes insoluble in it and remains as suspension at the end of Polymerization unlike conventional solution polymerization. The suspended polymers are separated by filteration as fine solid powders with the help of Buckner funnel using wattman 40 fitter paper.

A high degree of conversion (80-90%) was obtained. It was found that mother liquor (i.e. filtrate) contains 0.5 to 3.0 wt% EA in toluene depend upon the ratio of MAA/EA taken, as confirmed by GLC technique. It was also found that EA% in mother liquor increases with the increasing amount of EA in the MAA/EA ratio. However this mother liquor can be used for further polymerization with out affecting the properties of the polymer formed.

2.4 POLYMER CHARACTERIZATION (Experimental & Results and Discussion)

2.4.1 Acidimetric Titration

Concentration of methacrylic acid (MAA) in these copolymers was determined by acidimetric titration of 0.5 wt% polymer solution in methanol against the standard solution of NaOH. Phenolphthalein was used as an indicator.

When solutions of these copolymers in methanol was titrated against the standard NaOH solution, the MAA content was found to be much less than amount of MAA incorporated in feed (Table 2.2). In the case of polymers having high molecular weight, not all carboxylic groups are available for neutralization, due to their presence in deep particle core. If sufficient time is given all of them will be neutralized but hydrolysis of the ester groups may occur to give higher acid value.

Table 2.2: Acidimetric Titration Data

Polymer Code	Feed concentration (mol %)			Copolymer Composition (Mol % of MAA) Acidimetric Titration
	MAA	EA	AMA	
P1	53.368	45.896	0.736	49.68
P2	58.270	41.000	0.730	54.76
P3	63.098	36.177	0.725	59.83
P7	62.983	36.110	0.907	58.25
P8	62.867	36.044	1.089	56.84

2.4.2 I.R. Spectral Studies

Infrared spectra of methacrylic acid - ethyl acrylate were recorded in Nuzol mull using Nicolet FTIR model 420 D spectrometer.

In the I.R. spectra of the copolymers broad bands are observed in 3464 to 3160 cm^{-1} due to -OH str. vibration of -COOH group of MAA and strong bands at 1706-1703 cm-1 due to carbonyl str. vibration of carboxylic acid groups. C-H def. (symm.) of methyl group at 1376 - 1375 cm^{-1} and splitting of C-O str. vibration into two peaks at 1270 - 1178 cm^{-1} were observed which are characteristic to PMAA.

A sharp peak was observed at 2927 to 2920 cm^{-1} due to C-H assymmetric stretching of CH_3 group of MAA. At 1020 - 1018 cm^{-1} a weak peak was appeared due to C-O-C str. of the ester group (Fig. 2.1 to 2.5).

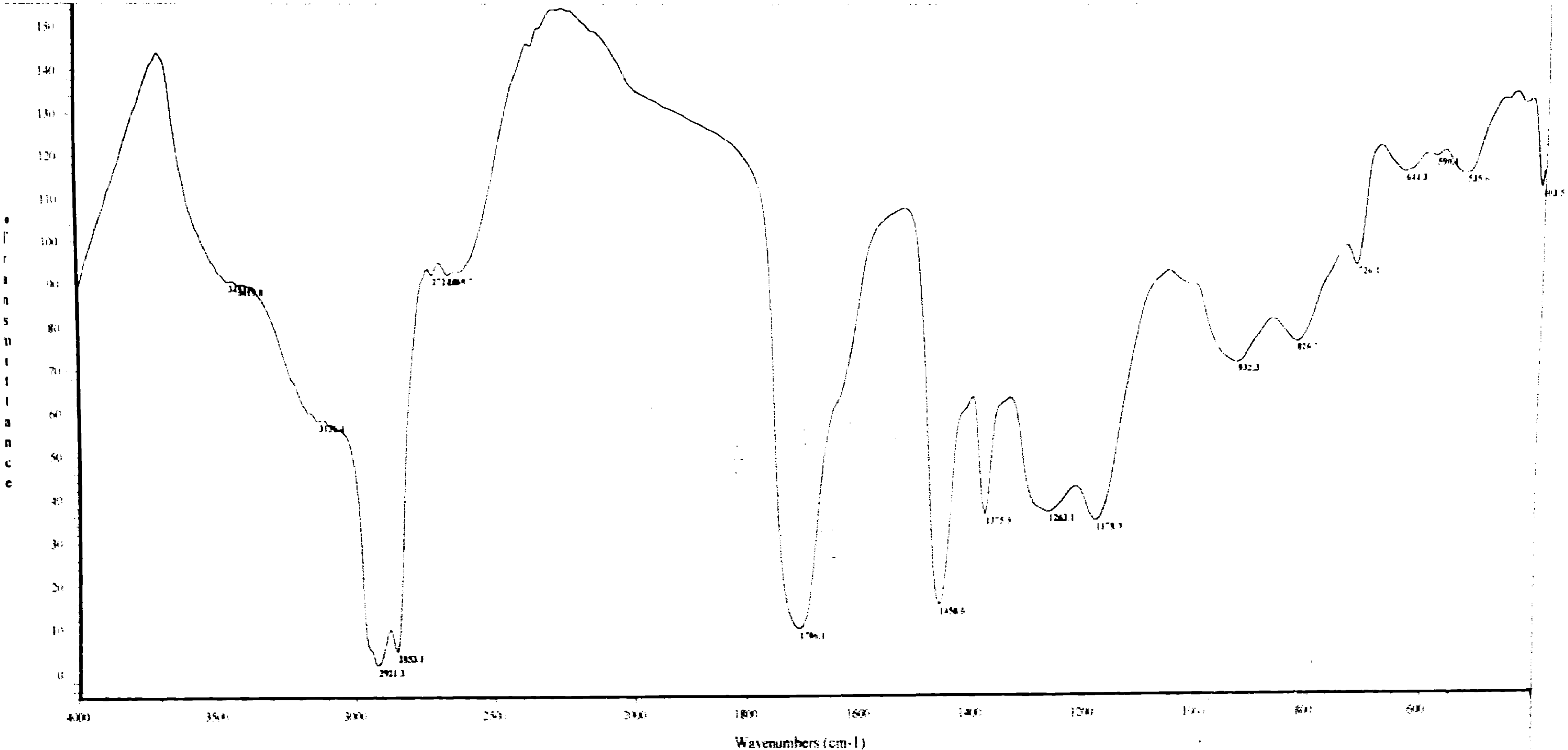

Fig. 2.1 I.R. Spectra of MAA-EA (50/50 w/w) Copolymer P1 Crosslinked with AMA (1wt%)

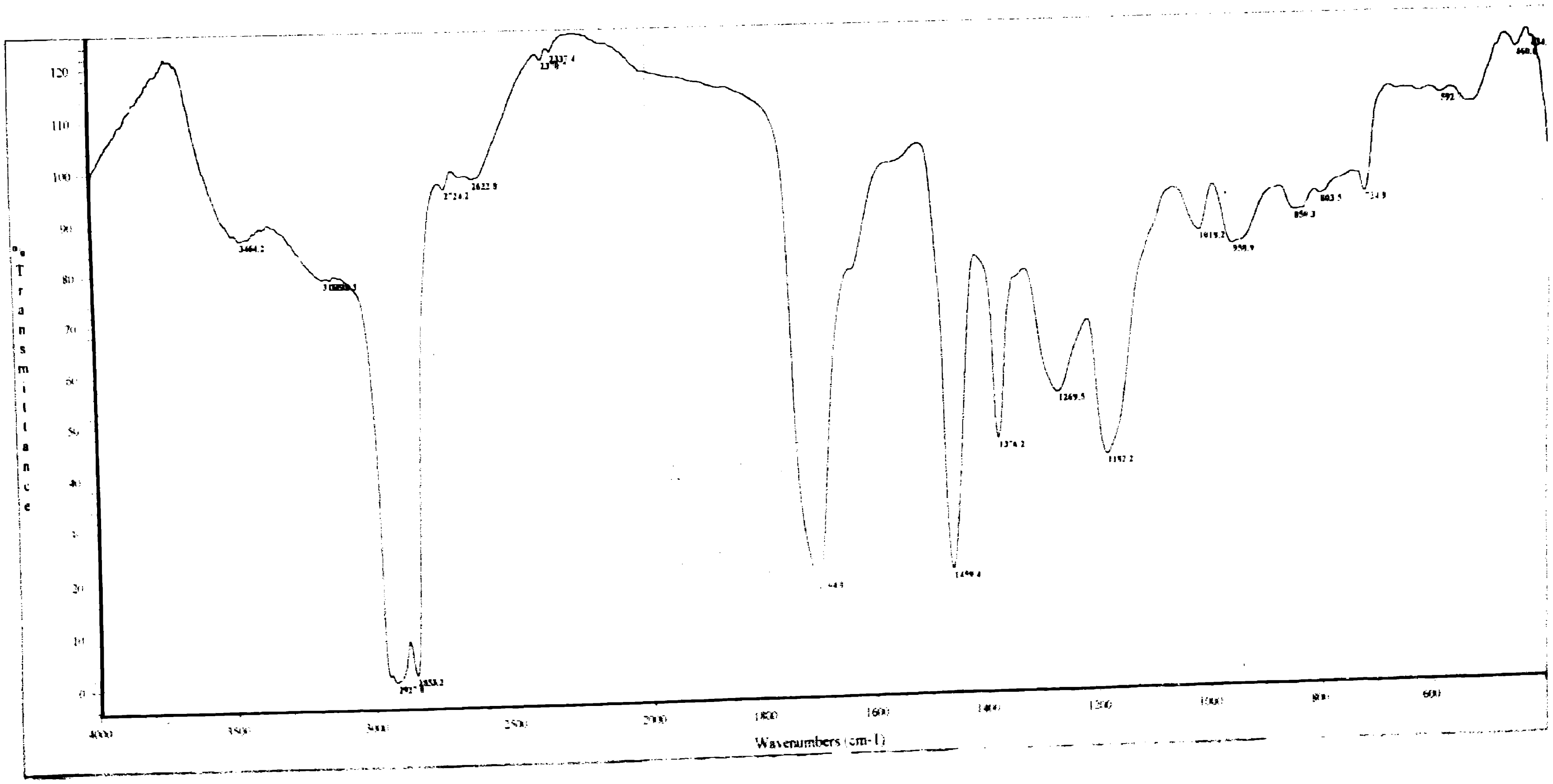

Fig. 2.2 I.R. Spectra of MAA-EA (55/45 w/w) Copolymer P2 Crosslinked with AMA (1wt%)

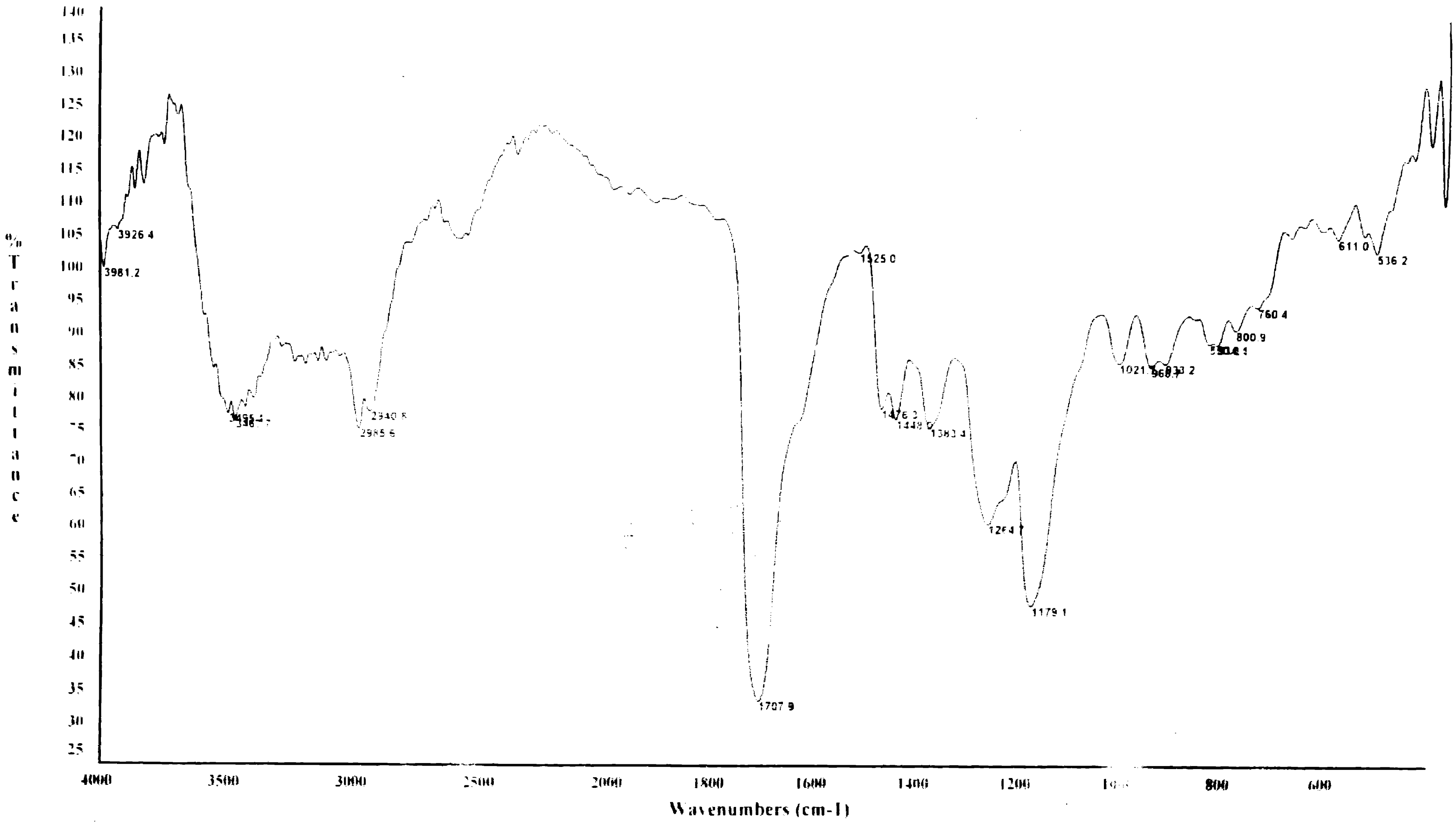

Fig. 2.3 I.R. Spectra of MAA-EA (60/40 w/w) Copolymer P3 Crosslinked with AMA (1wt%)

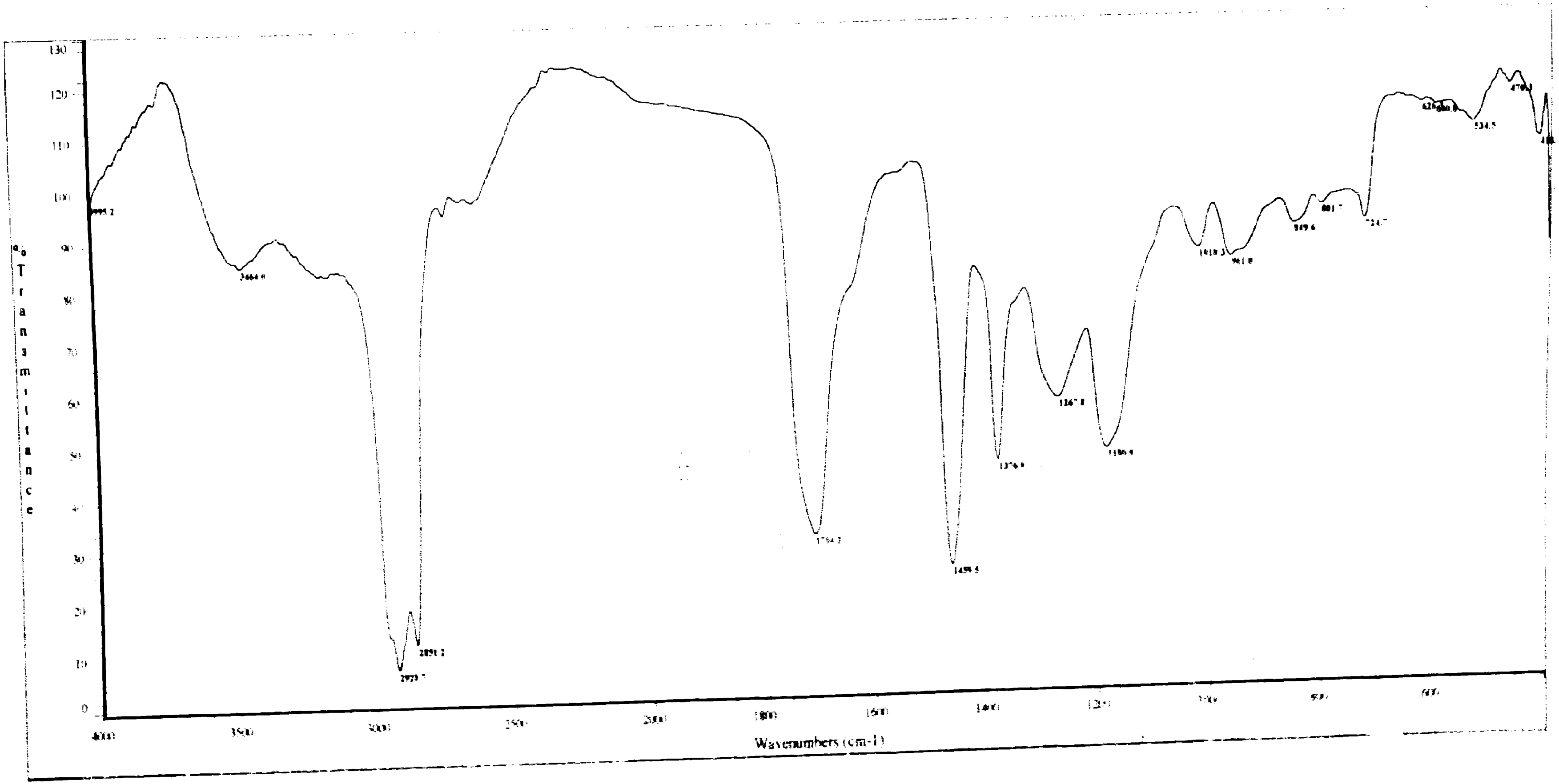

Fig. 2.4 I.R. Spectra of MAA-EA (60/40 w/w) Copolymer P7 Crosslinked with AMA (1.25wt%)

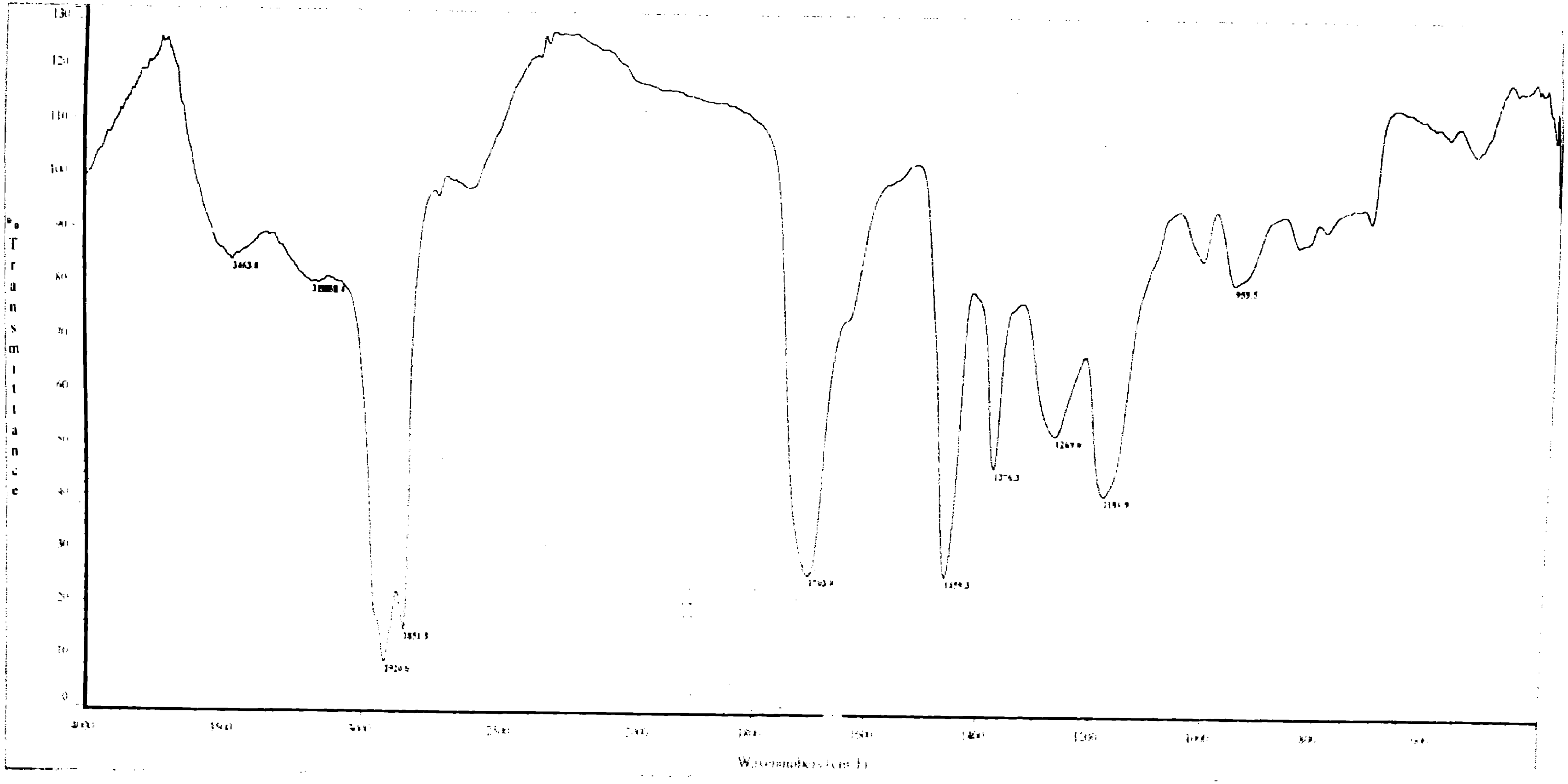

Fig. 2.5 I.R. Spectra of MAA-EA (60/40 w/w) Copolymer P8 Crosslinked with AMA (1.50wt%)

CHAPTER - 3

RHEOLOGICAL STUDIES

3.1 INTRODUCTION

3.1.1. Phenomena of Viscous Flow

Rheology is, by definition, the science of deformation and flow of matter. Viscosity is defined as the property of resistance to flow exhibited with in the body of a material expressed in terms of a relationship between applied shearing stress and resulting rate of strain in shear. If a force per unit area S causes a layer of liquid at a distance x from a fixed boundary wall to move with a velocity v, the viscosity η is defined as the ratio between the shear stress S and the velocity gradient $\partial v/\partial x$ or rate of shear γ [22], i.e.

$$S = \eta (\partial v/\partial x) = \eta\gamma$$

If η is independent of the rate of shear, the liquid is said to be Newtonian or to exhibit ideal flow behavior (e.g. sugar solutions, lubricating and vegetable oils). Polymer solutions and melts exhibit non-newtonian behavior which means that the ratio of shear stress to shear rate varies with the shearing stress. Two types of deviation from newtonian flow are commonly observed in polymer solutions and melts. One is shear thinning or psuedoplastic behavior, a reversible decrease in viscosity with increasing shear rate. Shear thinning results from the tendency of the applied force to disturb the long chains from their favoured equilibrium conformation, causing elongation in the direction of shear. An opposite effect, shear thickening or dilatant behavior in which viscosity increases with increasing shear rate is not observed in polymers.

A second deviation from newtonian flow is the exhibition of a yield value, a critical stress below which no flow occurs. Above the yield value, flow may be either newtonian or non-newtonian.

The above effects are shear dependent but time independent. Some fluids also exhibit reversible time - dependent changes in viscosity when sheared at constant stress. Viscosity decreases with time in a thixotropic fluid increases with time in a rheopectic fluid, under constant shear stress.

Dynamic or absolute viscosity, best determined in a rotational type of viscometer with a small gap clearance, is independent of the density or specific gravity of the liquid sample. Brookfield viscometer is the most widely used instrument for measuring the viscosity of plastisols and other liquids of a thixotropic nature. The instrument measures shearing stress on a spindle rotating at a definite, constant speed while immersed in the sample. The degree of spindle lag is indicated on a rotating dial. This degree multiplied by a conversion factor based on spindle size and rotational speed, gives a value for viscosity in centipoise. By taking measurement at different rotational speeds, an indication of the degree of thixotropy of the sample is obtained [78].

3.1.2 Rheology of Synthetic Thickeners

Performance of a printing paste is mainly governed by the rheological behaviour of the thickener used to prepare the printing paste. Viscosity or flow of a print paste not only affects the amount of paste to be applied but also the spread of the paste on the surface of and into the structure of the fabric. A good thickener should be pseudoplastic in nature. It is well known that all the natural thickeners and acrylic copolymer thickeners are pseudoplastic in nature. Thickeners can be classified as short flow or long flow depending whether it flows down a glass rod or not.

High molecular weight natural thickening agents, because of their molecular size and network of chains, form a type of spatial lattice in the aqueous medium. This results in the generation of viscosity. In synthetic thickeners, the thickening effect is produced by neutralizing the carboxylic acid groups with monovalent hydroxides like ammonium hydroxide. By the addition of ammonium hydroxide the synthetic thickener solution in water, ionic ammonium carboxylate form. Because of electrostatic forces of repulsion, the thickeners swells many times to its original size.

Most of the synthetic thickeners used in textile printing are thioxotropic in nature, which is estimated in terms of shear thinning index (STI). Viscosity of the synthetic thickeners is not only shear dependent but is pH dependent also. The addition of bases beyond the neutralization point leads to a reduction in the viscosity due to precipitation of polymer chains owing to the common ion effect. The cross linked polymer gives a printable viscosity at lower solid content than is required in case of linear polymers. Cross linked polymers can not dissolve but they swell considerably. Due to the swelling property these cross linked polymers give higher viscosity than the linear polymers.

In the present chapter, the rheological behaviour of methacrylic acid - ethyl acrylate (MAA-EA) copolymers cross linked with allyl methacrylate (AMA) has been reported. Polymers of varying MAA/EA ratio and degree of cross link density of AMA were synthesized for studying their rheological behaviour. Thirty polymer were synthesized in the laboratory, here only nine polymers (best of them) are taken for the rheological study.

3.2 STUDY OF RHEOLOGY (Experimental, Results and Discussion)

3.2.1 Brookfield Viscosity of MAA-EA Copolymers

Flow properties of the thickeners were measured by using Brookfield RVT viscometer at room temperatures. Brookfield viscometers are used for measuring viscosity based on the principles of rotational rheology. A 28% solution of ammonia (in different quantities) was used to thicken the aqueous solution of thickener and to vary the pH of the thickener paste in water.

The 1% powder of copolymers (P1 to P5) were mixed with water and the pH was raised to 7.5 to 8.2 by the addition of liquor ammonia. The viscosity of these solutions was measured at 20 rpm, at room temperature (Table 3.1, fig. 3.1).

Table 3.1: Effect of Copolymer Composition on Brookfield Viscosity

Polymer Code	Copolymer Composition						Brookfield Visosity (PS)
	MAA		EA		AMA		
	Wt%	Mol %	Wt%	Mol %	Wt%	Mol %	
P1	49.50	53.368	49.50	45.896	1.0	0.736	56
P2	54.45	58.270	44.55	41.000	1.0	0.730	112
P3	59.40	63.098	39.60	36.177	1.0	0.725	200
P4	69.30	72.547	29.70	26.738	1.0	0.714	92
P5	99.00	99.315	0.00	0.000	1.0	0.685	24

All the polymers (P1 to P5) were cross linked with 1 Wt% of allyl methacrylate (AMA). From the table 3.1, the viscosity was found to increase from 56 to 200 poise with an increase in the acidic comonomer content of the copolymer from 53.368 (P1) to 63.098 (P3) mol % and thereafter, it decreases to 24 poise in the copoloymer containing 99.315

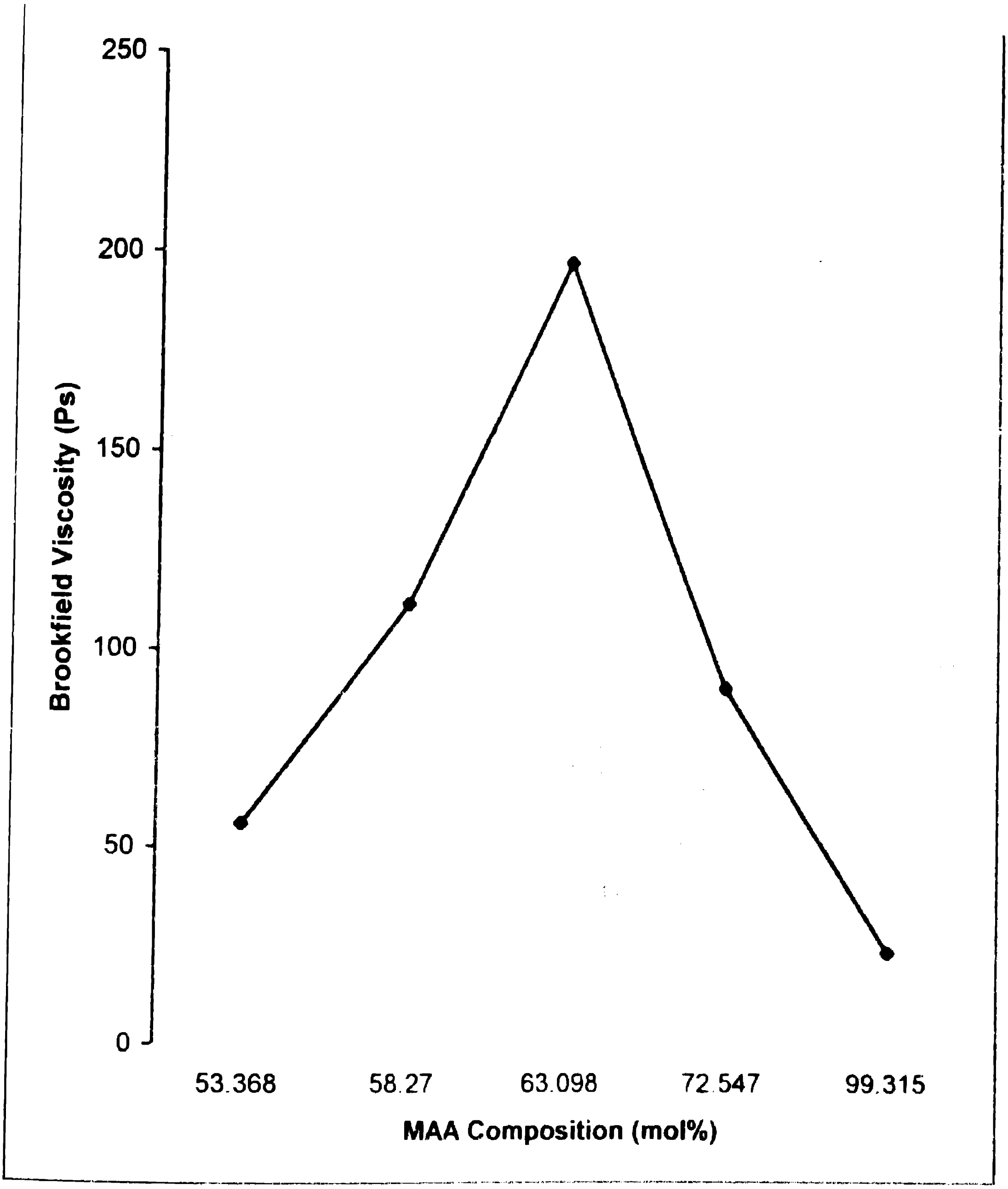

Fig. 3.1 : Effect Of Copolymer Composition On Brookfield Viscosity

(P5) mol% of acid. From these results it appears that 63.098 mol% of MAA is the optimum concentration beyond which any increase in the MAA concentration leads to decrease in the viscosity. On the addition of ammonia, ionization of the carboxylic acid groups takes place, resulting in the generation of charged ammonium carboxylate groups. Polymer chains extend due to the repulsion between the similar charges, leading to an increase in the viscosity. At a very high concentration of methacrylic acid these ammonium carboxylate groups may lead to dissolution of polymer into water rather than the chain extension, hence resulting in lower viscosity.

3.2.2 Effect of Cross Linking Agent Concentration on Viscosity

The cross linking agent concentration was varied from 0.75 to 1.75 wt% of comonomers for the optimum composition of MAA-EA (60/40 w/w). The Brookfield viscosity of all the cross linked polymers (P3, P6 - P9) (solid content 1%) was measured at 20 rpm and pH 7.5 to 8.2 (Table 3.2, fig. 3.2).

Table 3.2 Effect of Cross linking Agent Concentration on Viscosity

Polymer Code	Copolymer Composition						Brookfield Viscosity (PS)
	MAA		EA		AMA		
	Wt%	Mol %	Wt%	Mol %	Wt%	Mol %	
P6	59.55	63.214	39.70	36.243	0.75	0.543	40
P3	59.40	63.098	39.60	36.177	1.00	0.725	200
P7	59.25	62.983	39.50	36.110	1.25	0.907	250
P8	59.10	62.867	39.40	36.044	1.50	1.089	340
P9	58.95	62.751	39.30	35.978	1.75	1.271	550

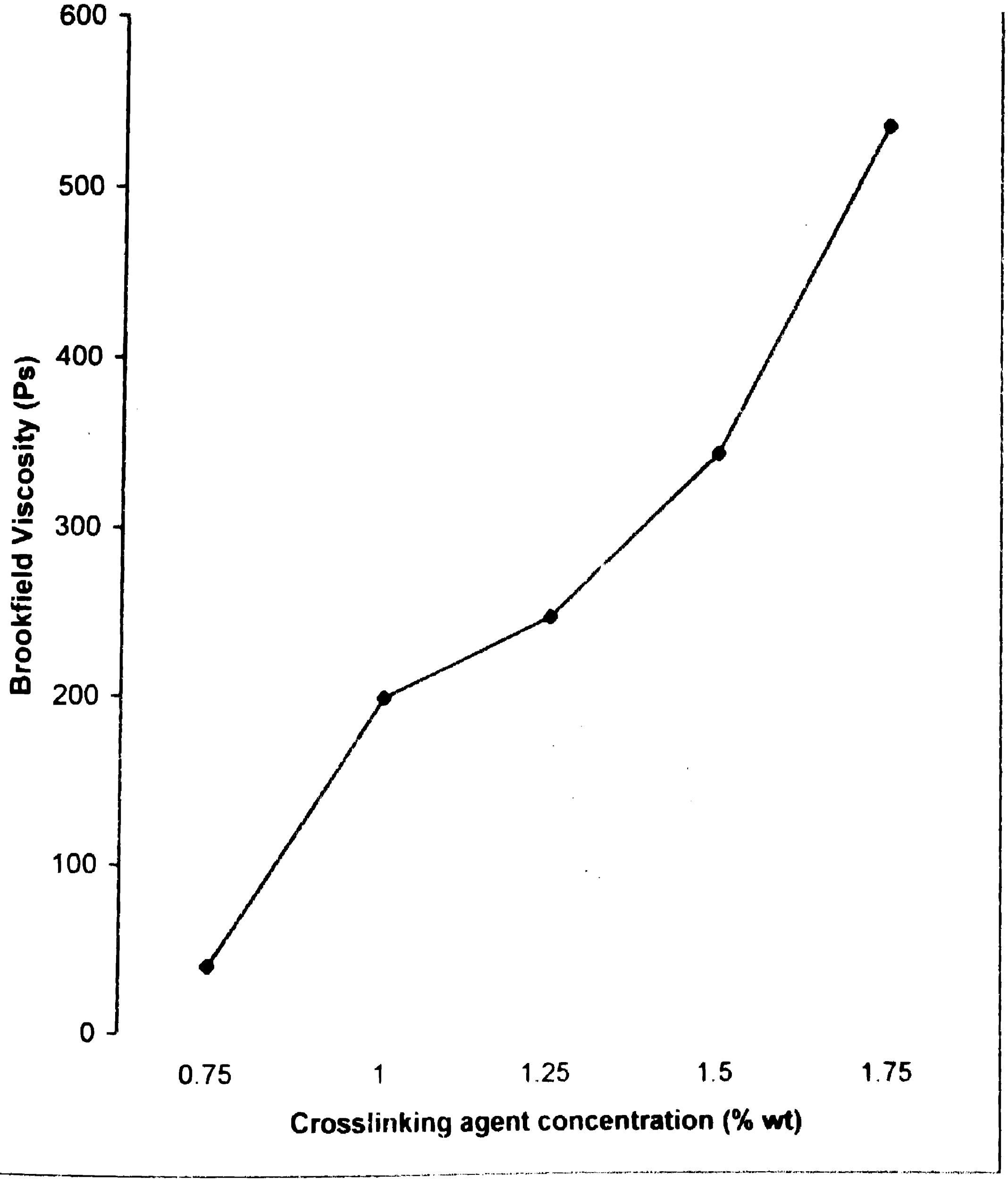

Fig. 3.2 : Variation Of Brookfield Viscosity With Copolymer Composition At Different Crosslinking Agent Concentration

Brookfield viscosity increases from 40 Ps to 550 Ps with increase in the concentration of cross linking agent from 0.75 to 1.75 wt%

3.2.3 Gel Content of Cross Linkea Polymers

Gel content of cross linked polymers was measured gravimetrically. 5 g of the solid polymer was mixed with 100 ml of methanol and kept at 40^0 C for 48 hours. After 48 hours, the mixture was centrifuged at 10,000 rpm at room temperature using Indian Equipment Corporation (IEC) high speed centrifuge. The swollen gel was washed with fresh methanol for 2-3 times to remove sol and centrifuge again. The gel was then dried in a oven at 100^0C and weighed.

An idea of the degree of the cross linking of the polymer was determined from the gel content of the polymer. It was found that the gel content increases from 34.3% to 80.3% with increase in the amount of cross linking agent AMA from 0.75 to 1.75 wt% (table 3.3, Fig. 3.3a).

Brookfield viscosity increases from 40 to 550 Ps with increase in gel content from 34.3 to 80.3% of the cross linked polymers (fig. 3.3b).

Table 3.3: Effect of Gel Content on Viscosity

Polymer Code	Gel Content %	Brookfield Viscosity (PS)
P6	34.3	40
P3	48.7	200
P7	55.4	250
P8	64.0	340
P9	80.3	550

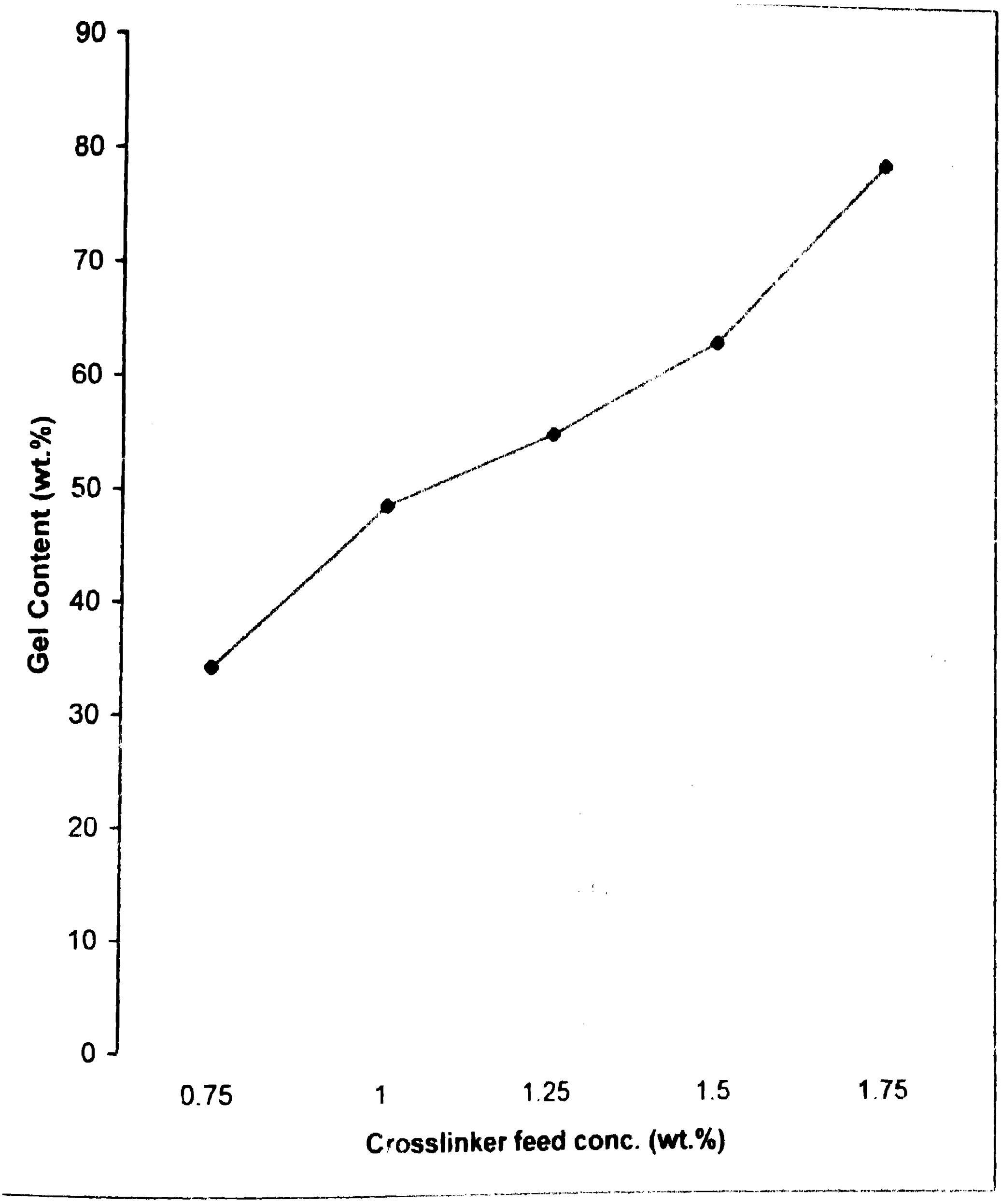

Fig. 3.3a: Plot Of Gel Content Vs Crosslinker (Allyl Methacrylate) Feed Concentration (Wt.%)

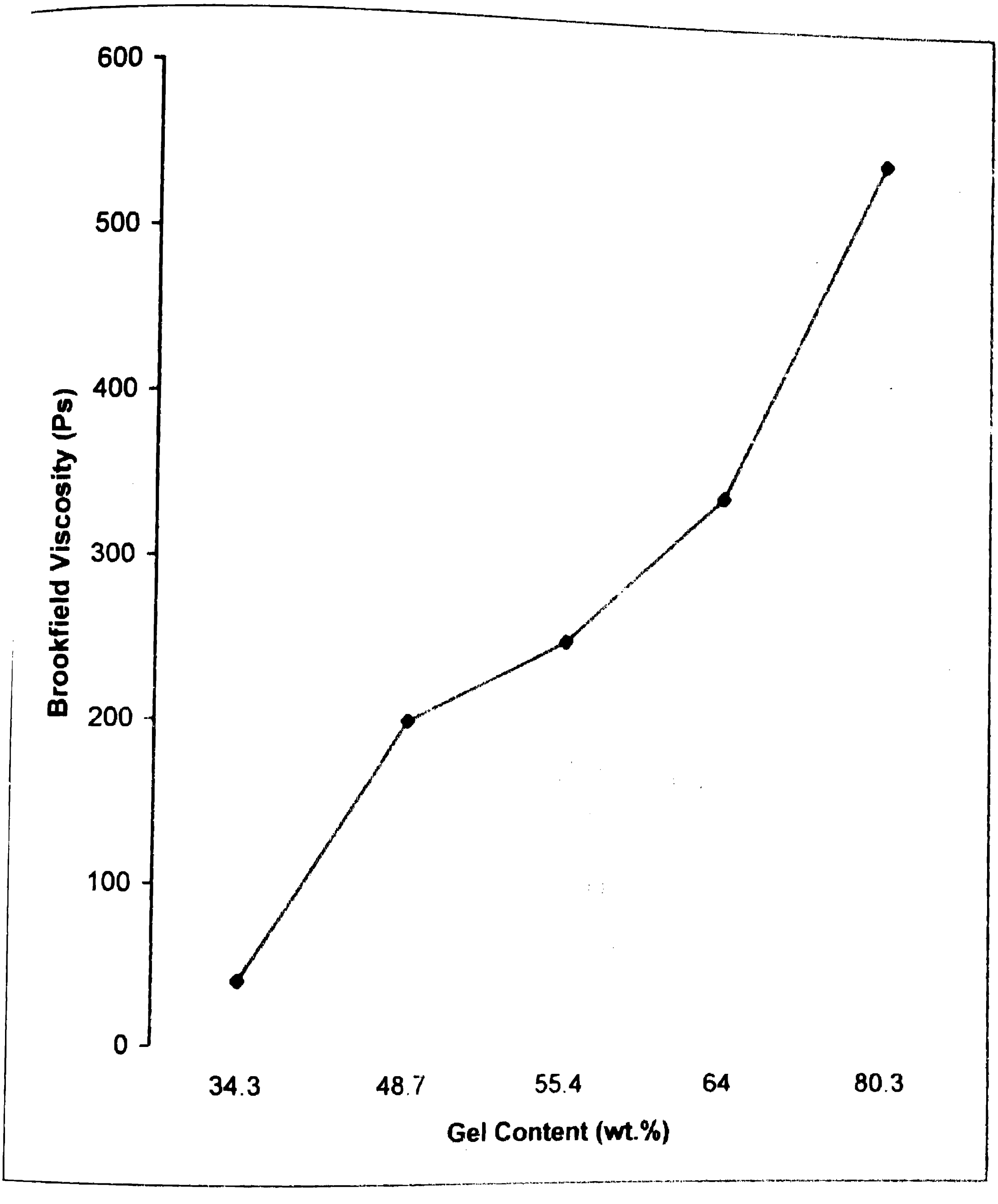

Fig. 3.3b: Effect Of Gel Content On Brookfield Viscosity Of Polymers Crosslinked With Allyl Methacrylate (Solid Content 1%)

3.2.4 Effect of Solid Content on Viscosity

Brookfield viscosity in the range 0.5 to 1.5% solid content was measured at 20 rpm at room temperature to study the effect of solid content of synthetic thickener on viscosity.

Brookfield viscosity increases with increase in the solid content of the polymer in all the cases (Table 3.4). The viscosity curve (fig. 3.4) showed a steep rise from 168 Ps at 0.5% solid (pH 7.5 to 8.2, 20 rpm, room temperature) to 240 and 435 Ps at a solid content of 1 and 1.5% respectively incase of P7 polymer. Similar behaviour was also observed in other cross linked polymers.

Table 3.4: Effect of Solid Content on Brookfield Viscosity

Solid Content (%)	Brookfield Viscosity (Ps)		
	P2	P3	P7
0.5	82	121	168
1.0	119	200	240
1.5	195	305	435

The polymer chains in a solution are completely enveloped by the solvent and there is a critical concentration at which no free solvent is left. Above this concentration, polymer chains are tightly packed together giving rise to a very high viscosity. In the present system, 1% solid content appears to be the critical concentration.

3.2.5 Effect of pH on Brookfield Viscosity

The Brookfield viscosity measurements were carried out at different pH (6-10.5) values. The concentration of the thickeners chosen was 1% for studying the pH dependency.

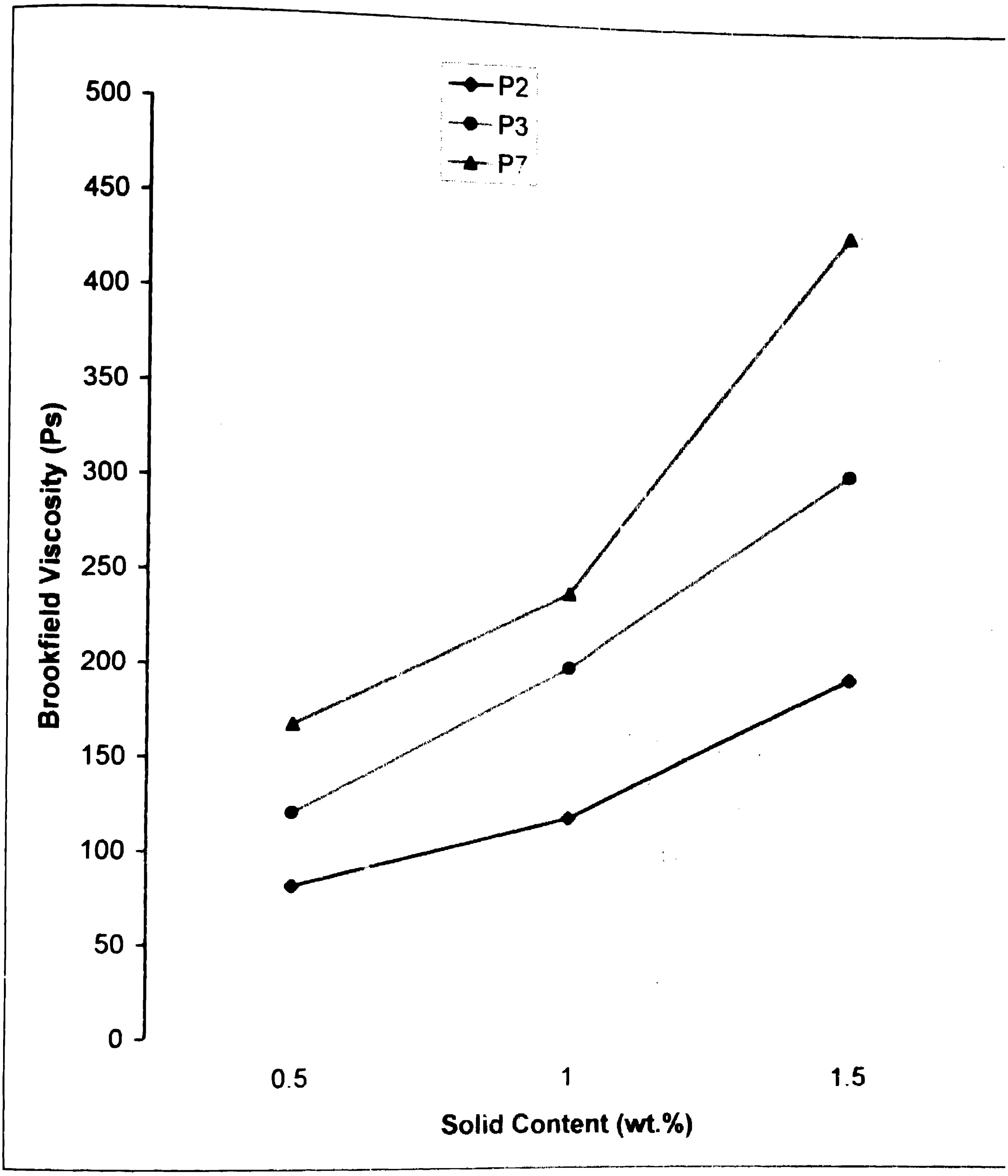

Fig. 3.4 : Variation Of Brookfield Viscosity With Polymer Concentration (Solid Content) Of Crosslinked (P2, P3 & P7) Polymers At pH 7.5-8.2.

Brookfield viscosity over a wide range of pH (6-10.5) (solid content 1%) was measured. Viscosity was found to increase with increase in the pH up to 8.2 and beyond that any increase in the pH led to fall in the viscosity (Table 3.5 to 3.7, Fig. 3.5 to 3.7).

Table 3.5: Effect of pH on Brookfield Viscosity of P2 at Different Shear Rate.

pH Value	Brookfield Viscosity (Ps) at Different RPM				
	2.5	5	10	20	50
6.3	472	268	160	98	54.4
7.1	496	284	172	106	59.2
8.1	536	308	180	112	60.4
9.2	480	280	168	104	58.4
10.1	464	276	164	100	56.0

Table 3.6 Effect of pH on Brookfield Viscosity of P3 at Different Shear Rate

pH Value	Brookfield Viscosity (Ps) at Different RPM				
	2.5	5	10	20	50
6.2	800	464	264	164	108
7.1	920	528	304	188	120
8.2	960	560	328	200	128
9.3	912	516	300	180	112
10.2	896	508	296	178	104

Table 3.7 Effect of pH on Brookfield Viscosity of P7 at Different Shear Rate

pH Value	Brookfield Viscosity (Ps) at Different RPM				
	2.5	5	10	20	50
6.2	960	590	330	205	122
7.2	1120	650	385	230	140
8.2	1180	690	410	250	150
9.3	1100	640	380	220	130
10.2	1080	630	375	215	126

Viscosity is related to coil density of the polymeric chains. When ammonia is added to the polymer dispersion in water, some ionization occurs, providing ammonium (NH_4+) counter ions and polymeric chains containing carboxylate ions. The negatively charged carboxylate ions will tend to agglomerate along side the chains which repel each other electrostatically. Because of this, polymer chains enlarge and viscosity increases. After complete neutralization, addition of more ammonia results in a build up of counterions of ammonium which leads to decrease in viscosity.

3.2.6 Effect of Shear Rate on Brookfield Viscosity

Brookfield viscosity in the range of 2.5 - 100 rpm was measured to study the effect of shear rate.

The effect of shear rate on Brookfield viscosity of four selected polymers (P2, P3, P7 & P8) was studied at 2.5 to 100 rpm (solid content 1%, pH 7.5 - 8.2) (Table 3.8, Fig. 3.8). The nature of all of them was found

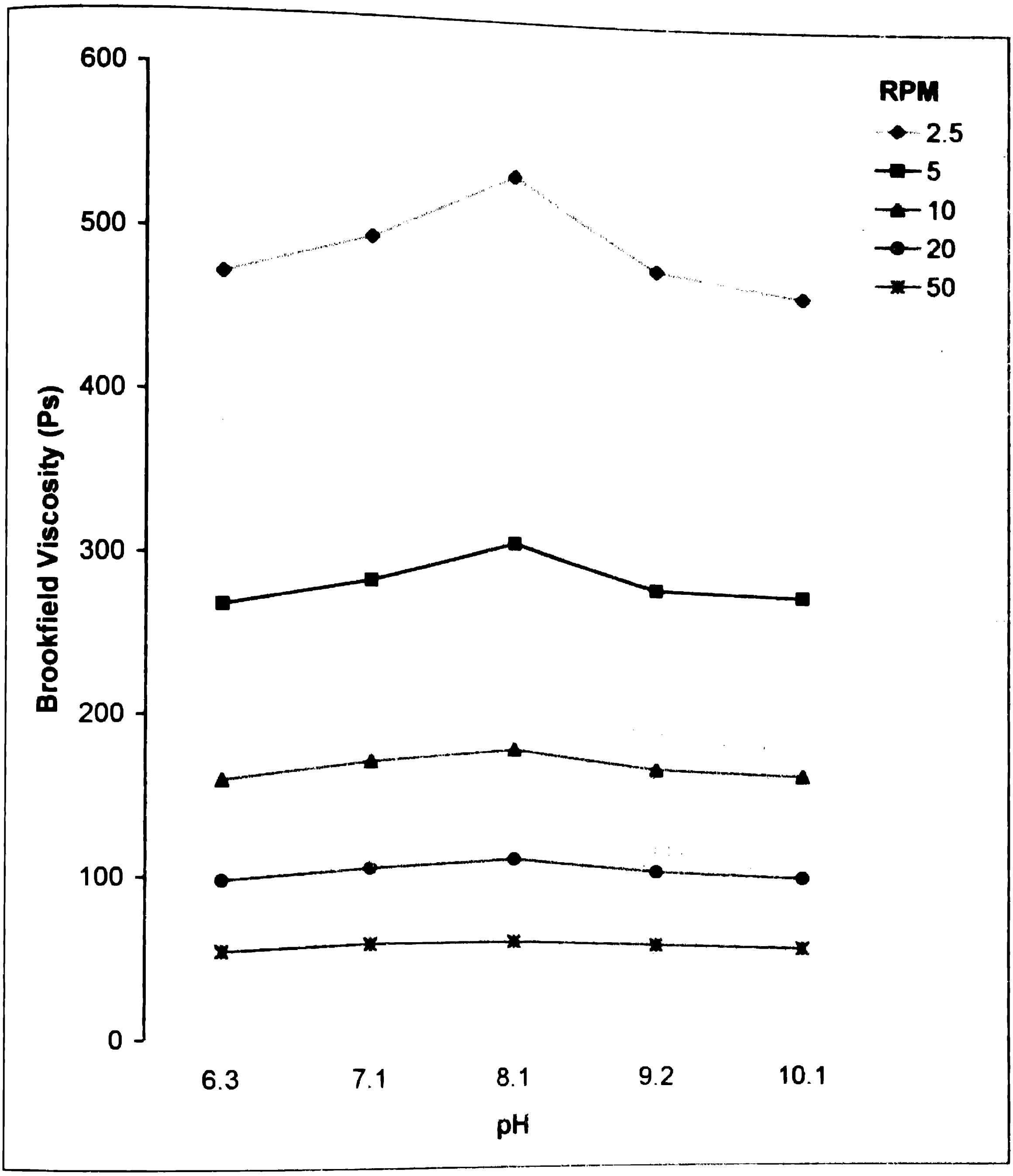

Fig. 3.5 : Effect Of pH On Brookfield Viscosity Of P2 (MAA - EA, 55-45 Wt.%) At Various Shear Rate (Solid Content 1%)

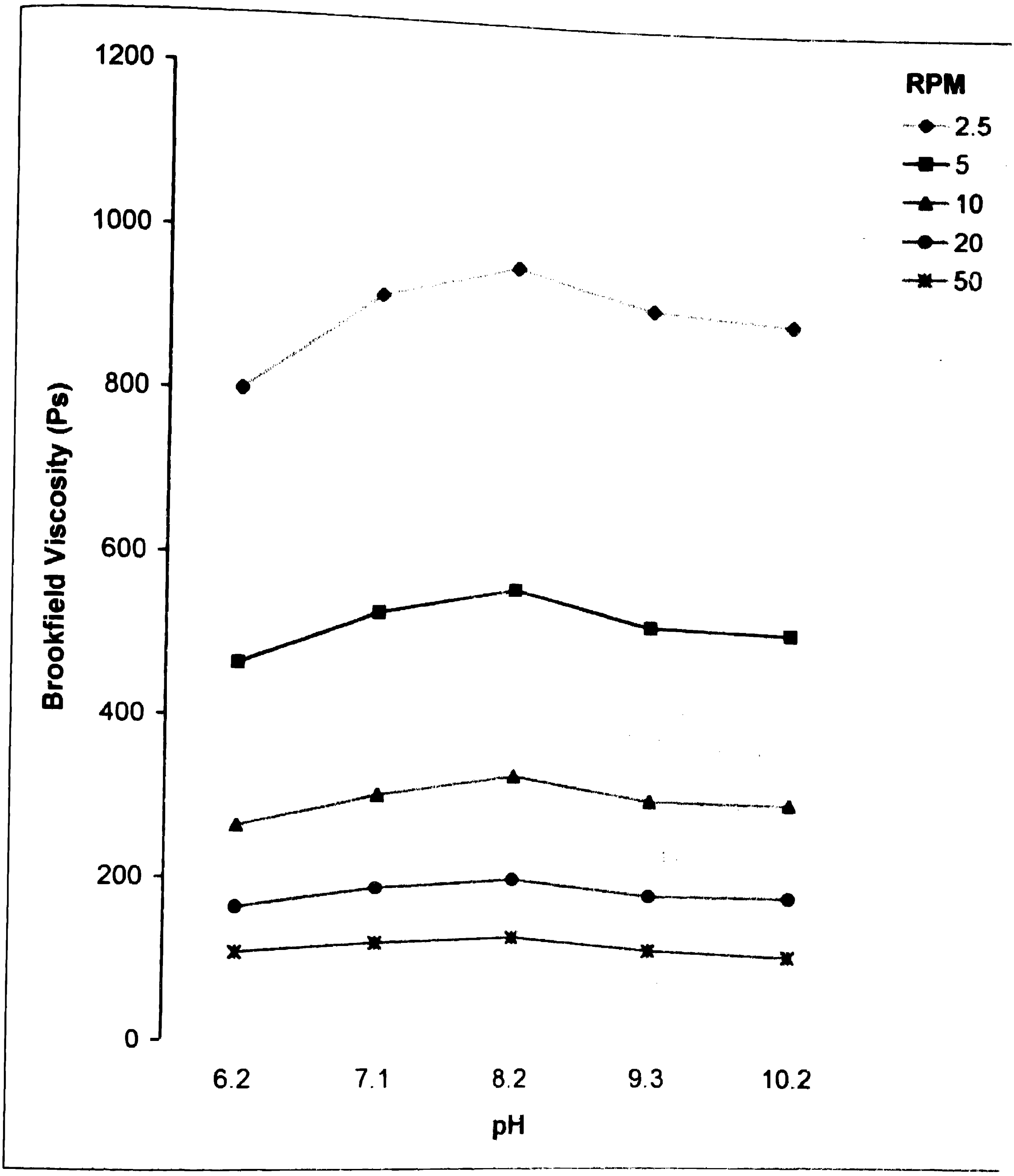

Fig. 3.6 : Effect Of pH On Brookfield Viscosity Of P3 (MAA - EA, 60-40 Wt.%) At Various Shear Rate (Solid Content 1%)

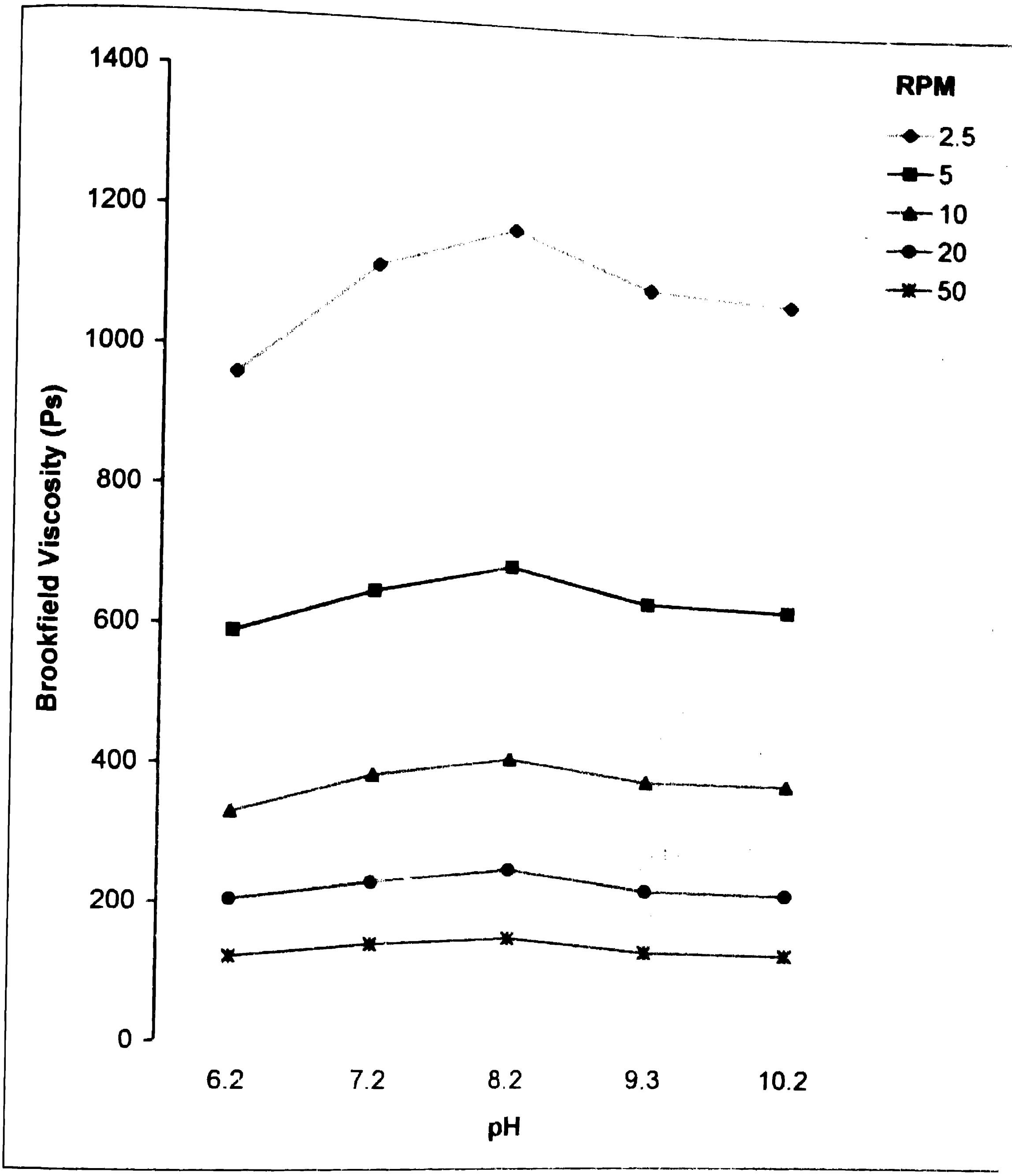

Fig. 3.7 : Effect Of pH On Brookfield Viscosity Of P7 (MAA - EA, 60-40 Wt%) At Various Shear Rate (Solid Content 1%)

to be pseudoplastic therefore they are suitable for thickening applications. The observed drop in the viscosity with increase in shear rate may be related to the break down of enveloped network polymer in the dispersions by mechanical action.

Table 3.8: Effect of Shear Rate on Brookfield Viscosity

RPM	Brookfield Viscosity (Ps)			
	P2	P3	P7	P8
2.5	536	960	1180	1440
5	312	650	690	920
10	188	340	410	570
20	112	200	250	340
50	68.8	112	150	179
100	30.2	70	90	116

3.2.7 Effect of Electrolytes on Viscosity

Brookfield viscosity was measured in the presence of 0.5-1.5% sodium chloride (NaCl).

Effect of electrolytes on Brookfield viscosity of four polymers (P3, P7 & P9) was measured at 20 rpm (pH 7.5-8.2, solid content 1%). Viscosity drops drastically on the addition of 0.5 to 1.5% NaCl (Table 3.9, Fig. 3.9).

Table 3.9: Effect of Electrolyte on Brookfield Viscosity

NaCl Concentration (Wt%)	Brookfield Viscosity (Ps)			
	P3	P7	P8	P9
0.0	200	250	340	550
0.5	36	42	37	40
1.0	17	21	15	18
1.5	12	13	7	9

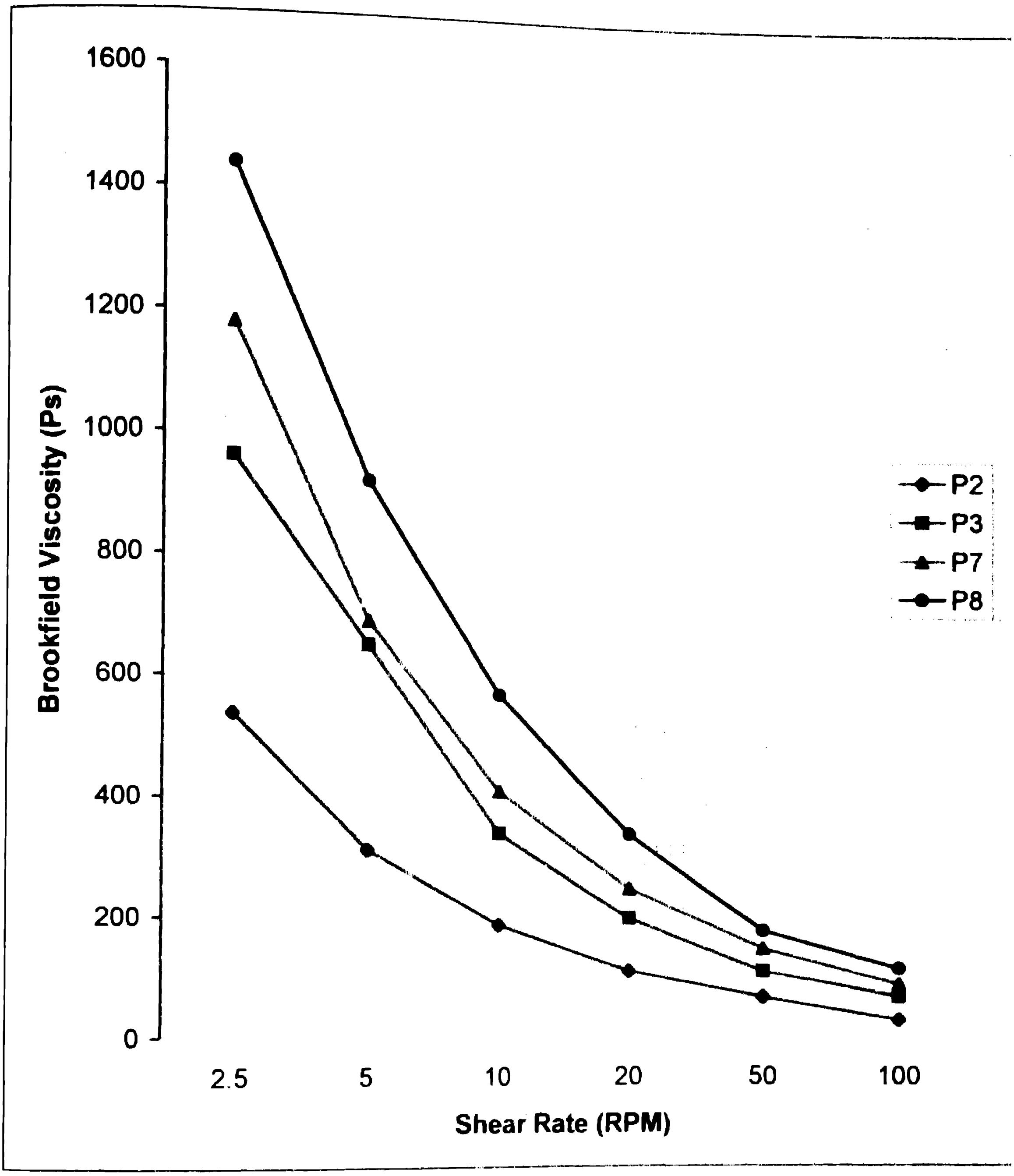

Fig. 3.8 : Variation Of Brookfield Viscosity Of Crosslinked Polymers With Shear Rate

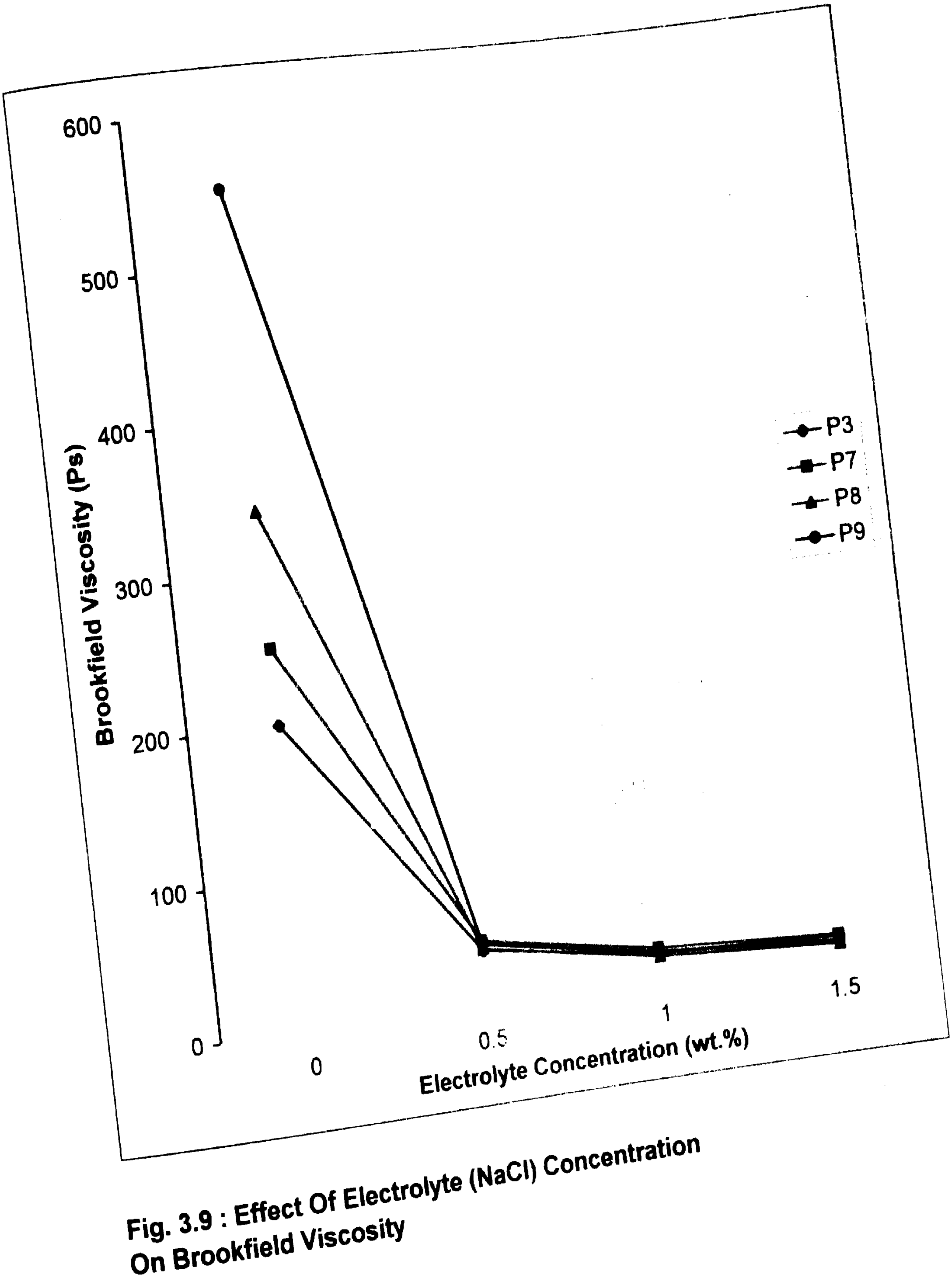

Fig. 3.9 : Effect Of Electrolyte (NaCl) Concentration On Brookfield Viscosity

The salt which is added externally, decreases the degree of dissociation through common ion effect, resulting in the drastic drop of viscosity . It was observed that the highly cross linked polymers, are more sensitive to electrolytes. In case of cross linked polymers, the extended polymers chains are swollen due to absorption of an excessive amount of solvent (water). Due to addition of salts, the extended polymers coils become recoiling resulting into desorption of water, which leads to loss in viscosity.

CHAPTER - 4

PERFORMANCE STUDIES

4.1 INTRODUTION

Pigments are molecular aggregates. The definition of pigment implies general insolubility and almost insolubility in water. Pigments suitable for pigment printing should have certain properties. For example, the shades produced should exhibit good fastness to light, washing, solvent and especially to abrasion (rubbing). The emulsion thickenings made by using them should give sharp impressions, develop good brilliancy and have good reproducibility.

Pigments do not posses any groups which can form bonds with fibres. Therefore pigments do not have any affinity for fibre. They require a binder for their fixation purpose. Pigments used in the textile industry are mainly synthetic organic materials, carbon block, titanium dioxide (for white pigments) and Copper & Aluminium alloys (for metallic bronze pigments). The suitability of pigments in pigment printing depends on the particle size, particle size distribution, degree of dispersion, specific gravity and solubility in solvents etc.

There are certain advantages associated with pigment printing. For example, the application procedure involving printing, drying and curing is a simple one without requiring any wet after treatments. It is applicable to all fibres. This include fibers like polypropylene & glass fibres, which can not be dyed with fibre substantive dyes. Extensive colour range with high light fastness is available in pigments. Shades matching is very easy in pigment printing. There are certain limitations also to balance against the substantial advantages of pigment printing. For example, desired fastness

to washing, rubbing and drycleaning is not always achieved and the feel of the pigment printed fabric may be affected.

In addition to the pigment, the printing paste contains thickeners, binder, cross linking agent and catalyst etc.

In this chapter, the performance of MAA-EA based synthetic thickener in pigment printing and comparison with Kerosene emulsion thickener and one of the commercially available synthetic thickener RAN 5000 is reported.

4.2 EXPERIMENTAL

4.2.1 Materials

4.2.1.1 Cotton Fabric

Cotton fabric was used for printing. It was scoured and bleached. It had the following specifications.

Warp count = 88 per inch

Weft count = 84 per inch

4.2.1.2 Printing Auxiliaries

TPI 2135 Binder of Vam Organic Chemicals Ltd. a melamine - formaldehyde based fixer of Colour Chem. Ltd. (CCL) and pigments Imperon Black KC-G, Imperon Blue KC-BN, Imperon Yellow KC-GG and Imperon Red KC-GR of Dystar (The Dyestuff company of Bayer and Hoechst), manufactured in India by Colour Chem. Ltd, Mumbai were used for printing. Diammonium hydrogen phosphate (DAP) of E. Merck was used as a catalyst in Kerosene emulsion thickener.

4.2.2 Stock Paste Formulations

(a) Kerosene Emulsion Paste

Table 4.1 : Kerosene Stock Paste (KE)

Ingredients	Parts
Binder	9
Water	15
DAP	1.5
Alphox 200	2
Kerosene	76

(b) Synthetic Thickeners

The 1% solid content of P3 was taken for the preparation of stock paste. The stock paste formulations for P3 and RAN 5000 are given in Table 4.2 and 4.3 respectively. Ammonium hydroxide solution (28%) was added to adjust pH to 7.2 - 8.2.

Table 4.2: For P3 Stock Paste

Ingredients	Parts
P3 Thickener	1
Water	89
Binder	9
Liquor NH_3	1
Total	**100**

Table 4.3: For RAN 5000 stock paste

Ingredients	Parts
RAN 5000	3.5
Water	87.5
Binder	9.0
Total	**100**

In case of RAN 5000, 3.5 parts of the thickener paste was added with 87.5 parts of water and 9 parts of Binder and left for half an hour to

swell. There is no need of ammonium hydroxide solution in case of RAN 5000.

4.2.3 Printing Paste Formulations

Printing paste formulations are given in table 4.4.

Table 4.4: Printing Paste Formulations.

Ingredients	Kerosene Emulsion (Parts)	Synthetic Thickener (Parts)
Pigment	3	3
Fixer	1	1
Stock paste	100	100
Total	**104**	**104**

With P3 & RAN 5000, the viscosity of the printing paste increased significantly on addition of black pigment, which was brought back to normal by the addition of 0.5 parts of ammonium sulphate.

4.2.4 Printing

Samples are screen printed with two squeeze strokes followed by drying of the printed samples at 105^0 C for 3 minutes and curing at 150^0C for 5 minutes.

4.2.5. Partial Substitution of Kerosene Emulsion

One blend of synthetic thickener (P3) and Kerosene (5 parts) was used in printing (Table 4.5)

Table 4.5: Partial Substitution of Kerosene

Ingredients	Parts
P3 Thickener	1
Kerosene	5
Water	84
Binder	9
Ammonium hydroxide sol.	1
Total	**100**

4.3 VISCOSITY OF STOCK AND PRINT PASTE

Brookfield viscosity of all the stock pastes and print pastes were measured at 20 rpm (Table 4.6). Stock paste of P3 was prepared at 1% solid content for achieving printable viscosity.

Table 4.6: Brookfield Viscosity of Stock Paste and Print Paste at 20 rpm.

Sample Code	Stock Paste Viscosity (Ps)	Print Paste Viscosity (Ps)			
		Red	Blue	Yellow	Black
KE	70	61	60	61	62
RAN	130	112	110	111	120
P3	134	115	112	114	121
P3KE	136	116	114	117	123

Brookfield viscosity of Kerosene emulsion and RAN stock paste was 70 and 130 poise respectively. Brookfield viscosity of P3 & P3KE stock paste was 134 & 136 poise respectively. When the pigment and fixer were added, drop in viscosity was observed as shown in Table 4.6.

4.4 EVALUATION OF PRINTED SAMPLES (Experimental, Results & Discussion)

The prints were evaluated in terms of brightness, wash fastness, dry & wet crock fastness and stiffness of the fabric (in terms of bending length).

4.4.1 Brightness of Printed Samples

The brightness of the printed samples was determined. A subjective rating was given 0 for poor and 5 for best.

Brightness of the prints obtained from P3 were found comparable to those obtained from RAN & KE system (Table 4.7). Printing paste containing some quantity of Kerosene provide for more bright prints in comparison to one aqueous based print pastes.

Table 4.7: Brightness of Fabric Printed with Different Thickeners

Polymer Code	Brightness Value			
	Red	Blue	Yellow	Black
KE	4	4.5	4.5	3.5
RAN	3.5	4	4	4
P3	4	4	4	4
P3KE	4.5	4.5	4.5	4.5

4.4.2 Fastness to Washing (ISO-3 & IS : 765-1979)

The wash fastness was tested using ISO test No. 3 specifications. A 10 x 4 cm size of printed test specimen was sandwiched between two

adjacent white fabric pieces. The prepared specimen was washed in a laundermeter using 5 gpl soap and 2 gpl soda ash solution at a temperature of 60^0 C for 30 minutes. The specimen was rinsed with cold water, dried at room temperature and evaluated.

Wash fastness properties of the prints obtained from laboratory synthesized thickener P3 were found comparable to those obtained from KE and RAN. Wash fastness in terms of change of colour came 4-5 on grey scale in case of all thickener systems. (Table 4.8).

Table 4.8 Effect of Different Thickeners on Wash Fastness Properties of the Fabric Printed with Different Pigments

Thickener Code	Wash Fastness Reading			
	Red	Blue	Yellow	Black
KE	4-5	4-5	4-5	4-5
RAN	4-5	4-5	4-5	4
P3	4-5	4-5	4-5	4-5
P3KE	4-5	4-5	4-5	4-5

4.4.3 Fastness to Rubbing (IS : 766-1956)

Dry and wet rub fastness of the printed samples were determined using Shirley crockmeter. The specimen was fixed to the rubbing devied such that the long direction of the sample follows the track of the finger of the crockmeter. The white rubbing fabric (5 x 5 cm.) was fixed to be end of the finger. The dry white rubbing fabric was rubbed to and fro ten times in 10 seconds on another specimen with a rubbing cloth that has been wetted

with water and having its own mass of water. The tested samples were dried and rubbing fastness rating were carried out.

Dry and wet rub fastness properties of the prints obtained from P3 were found comparable to those obtained from KE and RAN (table 4.9).

Table 4.9 Effect of Different thickeners on Crock Fastness (Dry & Wet) Properties of the Fabric Printed with Different Pigments.

Thickener Code	Rub Fastness Reading							
	Red		Blue		Yellow		Black	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
KE	4	3	4	3-4	4	3-4	3-4	2-3
RAN	4	3	3-4	3	4	3	3	2
P3	4	3-4	4	3-4	4	3-4	3-4	2-3
P3KE	4	3	3-4	3-4	4	3-4	3	2-3

4.4.4 Measurement of Stiffness (IS : 6490-1971)

It was measured in terms of bending length on Eureka bending length tester. The test specimen of 25 x 200 mm size were cut in the warp direction for the flat bed screen printed fabric samples. The sample was placed lengthwise on the plateform. Then bending length scale was placed over the specimen such that the zero of the scale coincides with the datum mark on the body of the instrument. The scale was pushed forward gently and slowly till the end of the sample was in line with two lines inscribed on acrylic sheets and the bending length was measured from the scale.

The sample printed with KE emulsion using red, blue and yellow pigments had the bending length in the range of 2.95 to 3.00 cm and in case of RAN, it was 3.2 to 3.3 cm (Table 4.10).

Table 4.10 Bending Length of Fabric Printed with Different Thickeners

Thickener Code	Bending length (in cm)			
	Red	Blue	Yellow	Black
KE	2.95	3.0	3.0	3.15
RAN	3.20	3.3	3.25	3.4
P3	3.25	3.4	3.3	3.45
P3KE	3.20	3.25	3.25	3.35ee

Bending length of unprinted fabric = 2.85 cm

The KE and RAN printed samples, had the bending length 3.15 cm and 3.4 cm with black pigment respectively. Bending length of the samples printed with P3 & P3KE were found comparable to that of RAN (Table 4.10).

CHAPTER- 5

SUMMARY AND CONCLUSIONS

5.1 SUMMARY AND CONCLUSIONS

In the present work synthesis of methacrylic acid (MAA) and ethyl acrylate (EA) copolymers cross linked with allyl metharylate (AMA) and their application in pigment printing of cotton fabric is reported. Synthesis of methacrylic acid - ethyl acrylate copolymer cross linked with allyl methacrylate was carried out using solution polymerization technique. The rheological properties of the polymers have been studied. Performance of the thickener in pigment printing has been reported with four pigments. A summary of the main findings discussed in the previous chapters is given below:

1. Polymerization of methacrylic acid - ethyl acrylate copolymers of various compositions along with AMA was carried out using solution polymerization technique.
2. Amount of cross linker (AMA) was varied from 0.75 wt% to 1.75 wt% keeping MAA - EA in 60:40 wt% ratio (optimum ratio of MAA-EA).
3. The polymers obtained were characterized for their composition using IR and acidimetric titrations. The concentration of MAA obtained from acidimetric titrations was found low.
4. In rheological studies, the rheological behaviour of these thickener was studied in terms of gel content, thickener concentration, pH of the medium, shear rate and electrolyte sensitivity on the Brookfield viscosity.

5. Viscosity increases with increase in gel content. High gel content polymers gives high viscosity but at the same time dullness in colour was observed as the gel content increases.

6. Maxima in Brookfield viscosity was observed in the pH range of 7.5-8.2 and thereafter it dropped on further increase in pH up to 10. This pH dependency of Brookfield viscosity was correlated with effective ionization of carboxylic acid groups.

7. It was noted that Brookfield viscosity of these thickeners undergoes a decrease on increasing the shear rate.

8. Among the various polymers, P3 was selected for printing application due to its ability to provide bright colour and sufficient viscosity.

9. Printing performance of synthetic thickener (P3) with four different pigments (red, blue, yellow and black) has been evaluated. The results obtained were compared with Kerosene emulsion and commercial RAN 5000 thickener. The fastness and Brightness properties of the prints with P3 gave comparable results with Kerosene and RAN 5000 emulsion, but feel of the prints were harsher than the Kerosene emulsion and comparable to RAN 5000 emulsion.

10. In order to improve the brightness of the fabric, 5 wt% of Kerosene was used in stock paste formulation. Results found was encouraging in terms of colour depth, brightness and feel of the fabric.

11. The prints obtained from P3KE were found to be much brighter; sharper and more uniform with all the pigments as compared to 100% synthetic thickener or 100% Kerosene emulsion thickener.

Performance of the synthetic thickeners in terms of colour depth, brightness, hand and fastness testify the potentiality of these MAA-EA based polymers as substitute of Kerosene in pigment printing of textiles.

REFERENCES

1. M.M. Gharia and Md. S. Rahman, Ahmedabad Textile Industry's Research Association, Ahmedabad, India, Report, p. 127-30.
2. H. Gutjahir, Textile Printing (edited by L.W. C. Miles), The Dyers Company Publication Trust, p. 143 (1981).
3. M.M. Gharia, M.M. Bhagwat, N.B. Patel et al, Colourage, p. 11 (July 1-15, 1990).
4. V.A. Shenai, Technology of Printing, Sevak, India, p. 400 (1990).
5. R. Seddon, Am. Dyest. Rep., p. 13 (Feb 1985).
6. W. Clarke and L.W.C. Miles, Rev. Prog. Color, 13, 27 (1983).
7. K.M. Shah, Hand Book of Synthetic Dyes and Pigments, Vol. III, p. 119 (1998).
8. R.M. Mittal and S.S. Trivedi, Colourage, P. 40 (Oct 22, 1981).
9. J.H.. Davids, Colour. Annu., p. 60 (1974).
10. P. Bajaj, R.B. Chavan & B. Manjeet, J. Macromol. Sci. - Rev. macromol. Chem. Phys., (24 (2) 387 (1984).
11. V.A. Shenai and N.M. Saraf, Colourage, p. 44 (October 1981).
12. M.M. Bhagwat and H. Srivastva, ATIRA Tech. Dig., 18 (3) 105 (1984).
13. R.B. Chavan , P. Bajaj and M. Goyal, Indian Jour,. Of Fibre and Textile Research, Vol. 19, p. 22 (March 1994).
14. B. Pravato, Simposium of Synthetic Thickeners, Sigma Prodotti Chimici S.P.A, p. 10 (July 1993).
15. K.. Dachs, Melliand Textilber, 50, 672 (1969).

16. P. Bajaj, M. Goyal and R.B. Chavan, J.M.S- Rev. Macromol. Chem. Phys., C 33 (3), 324 (1993).

17. J. Brandrup and E.H. Immergut (Eds). Polymer Handbook, Wiley - Interscience, New York p. VI/215-19 (1989).

18. G. Kanter, Am. Dyest Rep., 52 (1976).

19. R.B. Seymour, Introduction to Polymer Chemistry, Mc-Graw Hill, New York, p. 153 (1971).

20. D.N. Schulz, I. Duvdevani, J. Bock and E. Berluchi (Exxon Research and Engg Co.), U.S. Patent 4,650, 848 (1987); Chemical Abstr., 107, 78468 f (1987).

21. M.M. Bhagwat and H.C. Srivastva, ATIRA Tech. Digest, 18, 3, 105 (1984).

22. Fred W. Billmeyer, JR. Text Book of Polymer Sci., John Wiley & Sons, Singapore, p. 340 (1994).

23. I.G. Dammann (Cleanese Corp)., U.S. Patent US 4, 338, 239 (1982); Chem. Abstr, 97, 129076m (1982).

24. C. Haung, South African Patent ZA8, 306, 734 (1984); Chemical Abstr., 102, 115099f (1985).

25. S. Obayashi et al., European Patent EP 343, 490 (1989); Chem. Abstr., 112, 218, 075f (1990).

26. T. Kawame et. al (Kuraray Co.), Japanese Patent JP 01, 254 790 (1989); Chem. Abstr. 112, 119360b (1990).

27. F.J. Sehm (B.F. Goodrich Co), European Patent EP 371, 421 (199o); Chem. Abstr., 113, 1921 50v (1990).

28. Wiggins Michel (Henkel Co., USA), PCT Int. Appl., WO 98, 08, 89, Chem. Abstr., 128, 181102q (1998).

29. Iwasaki Masaki et al., European Patent EP 884, 334; Chem. Abstr., 66902e (1999).

30. Abraham Tonson et. al. (B.F. Goodrich Co.), U.S. Patent US 5, 475, 047 (1995); Chem; Abstr., 124, 147, 182 y (1996).

31. Brette Fwerruccio (3 v Inc., USA), U.S. Patent US 5, 861, 456 (1998); Chem, Abstr., 130, 126, 246 f (1999).

32. C.J. Chang et al (Rohn & Hacrylic Acids Co.), U.S, Patent US 4, 423, 199 (1983).

33. Allied Corp., Japanese patent JP 87, 57,408 (1987); Chem. Abstr., 107, 116453 g (1987).

34. G.C. Ruffner (Alco Standard Corp.), U.S. Patent US 4, 616 074 (1986); Chem. Abstr., 106, 822555 (1987).

35. T.G. Chemical Ind. Co., Japanese Patent JP 57, 108, 160 (1982); Chem. Abstr., 96, 15083n (1983).

36. D. Drahomir et al. (Roehm GmbH), Europian Patent EP 398, 151; Chem. Abstr., 112, 79, 372K (1990).

37. S. Gajdo et al, Romanian Patent RO 69,973 (1989); Chem. Abstr., 114, 83,813 p (1991).

38. N.V. Gandurina, N.S. Volkhonskaya et al Izv. Vyssh. Uchebh. Zaved., Tekhnol. Tekst. Promsti, 1, 58 (1986); Chem. Abstr., 105, 80, 494p (1986).

39. T.P. Karpriskaya, V.D. Malkov et al, USSR Patent 937, 468 (1982); Chem. Abstr., 97, 164,731t (1982).

40. N.S. Volkhonskaya, S.N. Veedeneeva, T.A. Deragacheva and L.I. Gandurin, Tekst. Promst., 7, 64 (1989); Chem. Abstr., 112, 20, 485e (1990).

41. R.P. Sivankova, M.A.. Lyubliner et al., USSR Patent 979, 551 (1982); Chem. Abstr, 98, 162, 373z (1983).

42. N.V. Gandurina, M.A. Didenko et al., Tekst. Promst., 1,57 (1981); Chem. Abstr, 94, 141, 065c (1981).

43. H. Norimasa et al., European Patent EP 19, 660 (1980); Chem. Abstr., 94, 158, 251q (1981).

44. Toyobo Co. Japanese Patent JP 59, 53,398 (1984); Chem. Abstr., 102, 168, 263 m (1985).

45. Yamada Kinij, Japanese Patent JP 59, 154, 133 (1984); Chem. Abstr., 102, 79,540c (1985).

46. M. Harold et al. (BASF), Ger. Offen. DE 4, 216, 318, Chem. Abstr., 120, 299552z (1994)

47. Garry Allan et al., U.S. Patent US 5, 703, 176; Chem. Abstr, 127, 109, 709 e (1997).

48. J. Hartmann et al. (BASF A.G.), Ger Offen. DE 3,641,700 (1987) Chem. Abstr., 107, 154957g (1987)..

49. T. Thomas et al. (Hoechst Co.) U.S. Patent US 4, 331,572 (1982).

50. Textile Dyer and Printer, 28, 5 (1990).

51. A. Bressiani (Sigma Prodotti Chimii S.R.L.), Frenh Demande FR 2,642, 077, Chem. Abstr., 114, 187, 506g (1991).

52. Bresciani Angelo, European Patent EP 640, 628; Chem. Abstr., 123, 170 588y (1995)..

53. Watt Peter et al., European Patent EP 721, 959; Chem. Abstr., 125, 170795e (1996).

54. Batty Norman et al., PCT Int. Appl., WO 9521, 797; Chem. Abstr., 124, 10175d (1996).

55. D.C. Blackley, Emulsion Polymerization , Applied Science Publishers Ltd., London, P. 4, 462-63 (1975).

56. Dr. P. Oldring and Dr. Plam (Eds.) Waterborn and Solvent Based Acrylics and their End User Applications, Vol. I, p. 41-44, 68-71, 80 (1996).

57. J.L. Guillaume, C. Pichot, J. Guillot, Jour. Poly. Sci. Polymer Chem., 26, 1937 (1988).

58. Kenneth J. Lissant (ed), Emulsion and Emulsion Technology, Part-II, Marcel Dekker, Inc., New York, p. 448 (1974).

59. T.C. Pan, J.F. Kuo, Jour. Polym. Sci, Polym. Chem. 29, 709 (1991).

60. Y. Zhang-Quing, L-Bag-Eng and Pan Z.R, Zzhejiang, Xaxue, Xuebao, Ziran Kexueban, 33 (1), 57 (Ch), (1999), Chem. Abstr., 131, 144899w (1999).

61. V.R. Gowariker, N.V. Viswanathan and Jayadev Sreedhar, Polymer Science, New Age Int. Limited, New Delhi, p. 73, 194, 204-206 (Sept, 1999).

62. G.G. Greth, J.Wilson, J. Appl. Polym. Sci., 5, 135 (1961).

63. G. Odian, Principles of Polymerization, Wiley - Interscience, New York, p. 336.

64. B. Robert et. al. (Wacker Chemic Gmbh), Ger. Offen. DE `97, 365736 (1999).

65. K. Hirashi et al. (Mitsui cyanamide), Japanese Patent JP 06, 166, 863; Chem. Abstr., 122, 12064z (1995).

66. T. Ogami and K. Komaki (Dainippon Ink and Chem.); Japanese Patent, JP 63,165,476 (1988); Chem. Abstr., 110 59, 481a (1989).

67. Z. Zhang, C. Wu and P. Jiang (Chinese Univ. of Sci. Tech.) Chinese patent, 1, 039,035 (1990); Chem. Abstr., 114, 24, 789q (1991).

68. M. Goyal, Ph.D. Thesis (1993), IIT Delhi, New Delhi, India.

69. Perronin Jean et al, U.S. Patent US 397 8016 (1976).

70. W.M. Kullicke, R. Kriewske, R.J. Muller, M. Prescher and H. Keller, Die Makromolecularen. Chemie, 142, 29 (1986).

71. S. Heimann, K. Dachs and Ludwighsafen, Melliand Textilber (Engl.. Ed.) p. 462 (1972).

72. Bresciani Angelo, European Patent, EP 0383057 (1990).

73. T. Schymitzck, T. Esche, H.K. Rouette, International Dyer, p. 17 (September 1997).

74. A.V. Gore and J. Varghese, Colourage, 29 (25), 3 (1982).

75. M.N. Chapatwala and Mantra, Colourage p. 19-20 (July 1991).

76. P. Bajaj, P.K. Gupta and Manjeet Bhatia, Colourage, p. 29 (August 21, 1986).

77. R. B. Chavan, P. Bajaj and Varsha, Colourage, 29 (20); 3 (1981).

78. Vishu Shah, Handbook of Plastics Testing Technology, John Wiley and Sons, New York, p. 174, 378 (1984).